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WASTE GUIDE FOR THE URANIUM MILLING INDUSTRY

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1962

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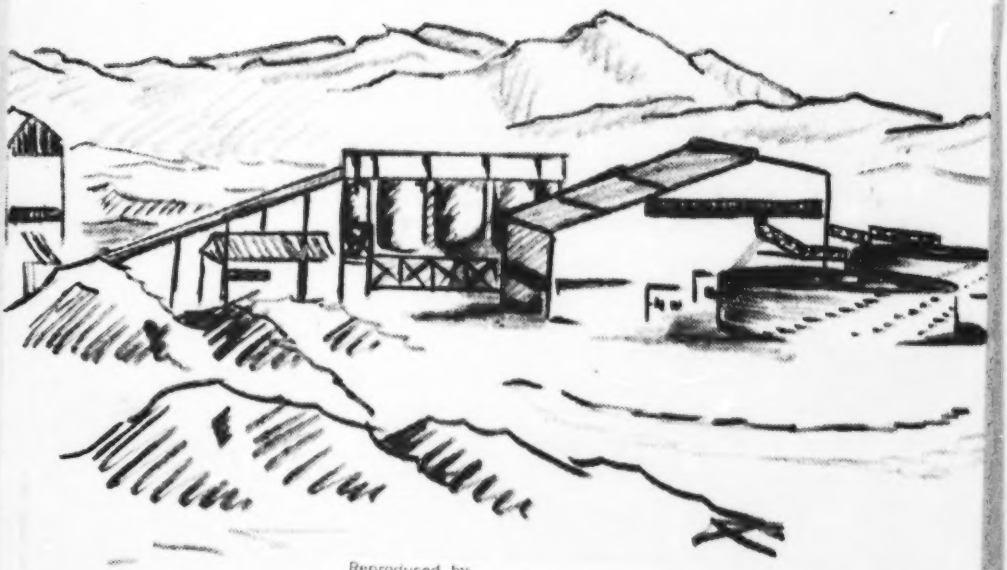

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WASTE GUIDE FOR THE URANIUM MILLING INDUSTRY

by

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U. S. Department of Health, Education, and Welfare
Public Health Service
Division of Water Supply and Pollution Control

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1962

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CENTER PUBLICATIONS

The Robert A. Taft Sanitary Engineering Center is a national laboratory of the Public Health Service for research, training, and technical consultation in problems of water and waste treatment, milk and food safety, air pollution control, and radiological health. Its technical reports and papers are available without charge to professional users in government, education, and industry. Lists of publications in selected fields may be obtained on request to the Director, Robert A. Taft Sanitary Engineering Center, Public Health Service, Cincinnati 26, Ohio.

CONTENTS

	Page
FOREWORD	v
INTRODUCTION	1
Uranium Milling Industry	2
Raw Material - Uranium Ore	4
Radioactivity in Waste	5
MILL PROCESSES	9
Ore Receiving, Crushing, and Sampling	9
Grinding	9
Uranium Extraction	10
Liquid-Solid Separation	11
Uranium Recovery	12
Ion Exchange (IX)	13
Solvent Extraction (SX)	14
Upgrading	14
PROCESS WASTES	21
The Mill Balance	21
Radium-226	26
Acid Leach - RIP	28
Acid Leach - Solvent Extraction	29
Alkaline Leach	30
Summary	31
Gross Alpha Radioactivity	32
Radium as Per Cent of Gross Alpha Radioactivity	35
Thorium	36
Uranium	37
Waste Solids	38
Water Usage	38
Chemical Characteristics	40
Alkaline Leach Process	40
Acid Leach Process	41
Ion-Exchange Recovery	42
Solvent Extraction Recovery	44
POLLUTIONAL EFFECTS OF WASTE	45
Radiological Pollutants	45

Radium 46
Chemical Pollutants 50
Effects on Stream Biota 50
Effects on Water Uses 53
Physical Pollutants 55

POLLUTION ABATEMENT METHODS 57

Tailings Ponds 58
Chemical Treatment 63
Waste Neutralization 63
Barite Treatment 64
Raffinate Treatment 65
Deep-Well Injection 67
Solid Waste Disposal 68

SUMMARY AND CONCLUSIONS 71

Uranium Milling Industry 71
Process Wastes 72
Pollutional Effects 72
Mill Waste Treatment 73
Conclusions 73

BIBLIOGRAPHY 75

FOREWORD

Beginning in late 1957, the Public Health Service undertook a series of in-plant surveys of uranium mills for the purpose of developing detailed information regarding the characteristics of wastes resulting from the extraction of uranium from its ores. Although primary interest has been in the radioactive wastes, especially Radium-226, data regarding the chemical characteristics and toxicity of the wastes were also obtained. Field studies of the fate of these wastes in the water environment and their effects on water quality were also conducted. This waste guide is a compilation of the findings of these studies, and has resulted from the efforts and generous cooperation of many persons, companies, and agencies.

The studies referred to here were conducted by the Radiological Pollution Activities Unit, Division of Water Supply and Pollution Control, Robert A. Taft Sanitary Engineering Center. They were made possible by the participation and cooperation of the Health Departments and Water Pollution Control Agencies of a number of States, the companies that operate the uranium mills, and other Federal agencies. Especially, the studies could not have been completed without the cooperation and assistance of the

Arizona State Department of Health
Colorado State Department of Public Health
New Mexico Department of Public Health
South Dakota State Department of Health
Utah State Department of Health
Wyoming State Department of Public Health

and the

Climax Uranium Company
Gunnison Mining Company
Homestake-New Mexico Partners
Homestake-Sapin Partners Company
Mines Development, Inc.
Uranium Reduction Company
Vanadium Corporation of America

and of the

Grand Junction Operations Office of the
U. S. Atomic Energy Commission

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Aerial view of a uranium mill in the Grants - Ambrosia Lake area of New Mexico. Its design capacity of 3,300 tons of ore per day is the largest of any United States mill. Approximately 350 acres of ponds are used to receive liquid and solid mill wastes. (Photograph courtesy of Kermac Nuclear Fuels Corporation)

WASTE GUIDE FOR THE URANIUM MILLING INDUSTRY

INTRODUCTION

The relatively recent growth of uranium mining and milling to its present position as a major industry in the United States has accentuated problems associated with disposal of its waste materials. In recognition of the importance of safe disposal of the wastes from this industry the United States Public Health Service and the Atomic Energy Commission have studied this matter extensively. Since 1957 the Public Health Service has examined in detail the various uranium extraction processes in use and the effectiveness of waste control measures in minimizing the discharge of harmful materials.[1-6] In addition, the effects of uranium mill waste discharges on the aquatic environment, the fate of these wastes in the stream, and the resulting radiological hazards to downstream water users have also received attention.[7-9] As a result of these investigations as well as studies carried out by others, a considerable body of information concerning uranium milling wastes has been developed. It is the purpose of this industrial waste guide to gather together this material and present a definitive analysis and characterization of the wastes which can be expected from uranium mills. The guide is intended primarily for the use of public health and water pollution control agencies, mill operators, and others in their efforts (1) to evaluate the potential hazards associated with mill wastes, (2) to determine the effectiveness of existing mill waste control practices, (3) to estimate the effect of future mills on their local stream environment and locate mill sites so as to minimize such adverse effects, and (4) to find more effective methods of waste control and treatment.

URANIUM MILLING INDUSTRY

The function of uranium mills is to extract uranium in concentrated form from ore deposits containing this element in quantities generally ranging from four to six pounds (as U_3O_8*) per ton of ore. Many such ore deposits are located in the Colorado Plateau area, and consequently, a number of the uranium mills are found in this area. Other important uranium-producing areas more recently developed in the United States are in central Wyoming, Ambrosia Lake in New Mexico, the western Dakotas, southern Oregon, northeastern Washington, and south Texas. Figure 1 shows the location of the uranium mills and provides an indication of the major ore-producing areas in the Western United States.

Mining of Colorado Plateau ores was started at the turn of the century for radium values, later for vanadium, and most recently for uranium. Since the early 1940's uranium ore pro-

Figure 1. Uranium mill locations.

* Uranium ore and mill product assays are conventionally expressed in terms of uranium oxide (U_3O_8) content. One pound of U_3O_8 contains 0.85 pounds of uranium (U).

duction has climbed steadily, and presently the United States is the world's largest producer of uranium ore and concentrate. In 1961 the United States produced 8 million dry tons of ore, more than twice the production four years earlier.[10] In spite of increasing production levels the Nation's undeveloped ore reserves remain high, the most recent estimate being 74 million tons containing U_3O_8 at an average concentration of 0.25%.

At the end of 1961 there were 25 active uranium mills (and two active concentrators) in the Western United States, as listed in Table 1. These mills, ranging in size from 200 to 3300 tons per day, had an aggregate design processing capacity of 20,800 tons per day. One additional mill under construction has an estimated capacity of 200 tons per day.

Table 1. URANIUM PROCESSING MILLS - 1961[a]

Company	Location of mill	Figure 1 code No.	Design ore capacity, T/day	Estimated cost of mill, $
Anaconda Co.	Grants, New Mexico	1	3,000	19,358,000
Climax Uranium Co.	Grand Junction, Colo.	2	330	3,088,000
Cotter Corp.	Canon City, Colo.	3	200	1,800,000
Dawn Mining Co.	Ford, Washington	4	400	3,100,000
Federal-Radorock-Gas Hills Partners	Fremont Co., Wyoming	5	520	3,370,000
Globe Mining Co.	Natrona Co., Wyoming	6	490	3,100,000
Gunnison Mining Co.	Gunnison, Colorado	7	200	2,025,000
Homestake-New Mexico Partners	Grants, New Mexico	8	750	5,325,000
Homestake-Sapin Partners[b]	Grants, New Mexico	9	1,500	9,000,000
Kermac Nuclear Fuels Corp.	Grants, New Mexico	10	3,300	16,000,000
Kerr-McGee Oil Industries	Shiprock, New Mexico	11	300	3,161,000
Lakeview Mining Co.[b]	Lakeview, Oregon	12	210	2,600,000
Mines Development, Inc.	Edgemont, South Dakota	13	400	1,900,000
Petrotomics Co.[c]	Carbon Co., Wyoming	14	200	1,500,000
Phillips Petroleum Co.	Grants, New Mexico	15	1,725	9,500,000
Rare Metals Corp. of America	Tuba City, Arizona	16	300	3,600,000
Susquehanna-Western, Inc.	Falls City, Texas	17	200	2,000,000
Susquehanna-Western, Inc.	Riverton, Wyoming	18	500	3,500,000
Texas-Zinc Minerals Corp.	Mexican Hat, Utah	19	1,000	7,000,000
Trace Elements Co.	Maybell, Colorado	20	300	2,208,000
Union Carbide Nuclear Co.	Rifle, Colorado	21	1,000	8,500,000
Union Carbide Nuclear Co.	Uravan, Colorado	22	1,000	5,000,000
Uranium Reduction Co.	Moab, Utah	23	1,500	11,172,000
Utah Construction and Mining Co.	Fremont Co., Wyoming	24	980	6,900,000
Vanadium Corp. of America	Durango, Colorado	25	750	813,000
Vitro Chemical Co.	Salt Lake City, Utah	26	600	5,500,000
Western Nuclear, Inc.	Jeffrey City, Wyoming	27	845	4,300,000
			22,500	$ 145,320,000
CONCENTRATORS				
Wyoming Mining and Milling Co.[c]	Natrona Co., Wyoming	28		
Union Carbide Nuclear Co.[b]	Green River, Utah	29		
Union Carbide Nuclear Co.[b]	Slick Rock, Colo.	30		
Vanadium Corp. of America	Monument Valley, Utah	31		
Vanadium Corp. of America	Naturita, Colo.	32		

[a]Reference 10.
[b]Inactive.
[c]Under construction.

On the basis of design capacity, 46 percent of the total domestic ore produced is milled in the Grants, New Mexico, area. The Colorado River Basin on the same basis accounts for 30 percent of the national total. In 1961 United States mills produced 17,399 tons of uranium oxide (U_3O_8) in concentrates which had an approximate gross industrial product value of $290 million dollars.

RAW MATERIAL - URANIUM ORE

Uranium-bearing ore, as it is delivered to the mills, may have a uranium content of from 0.1 to 1 or 2 percent as U_3O_8, and generally averages about 0.25 percent. This uranium is present as uranium-238 and uranium-235, both of which are naturally occurring radioactive parents of long chains of radioactive daughter products. Natural uranium contains about 99.28 percent uranium-238 and 0.71 percent uranium-235;[11] hence, the decay chain of uranium-238, known as the uranium-radium family of elements, is of primary concern. The decay scheme of this chain is shown in Figure 2. As presented in the figure, the parent element uranium-238, which has a half-life of 4.5 billion years, decays by alpha emission to thorium-234, which has a half-life of 24.1 days and in turn decays by beta emission to protactinium-234; the decay chain continues until stable lead-206 is reached. In all the series contains eight alpha emitters and six beta emitters. Two minor branches occur in the chain, but are not shown since their effect is negligible.

The majority of ores contain this radioactive family of elements in secular equilibrium, i.e., the daughter products are being formed at the same rate at which they are decaying, with the amount of any member actually present remaining constant. Roughly, one million years are required for pure uranium to reach equilibrium. Selective natural leaching from the ore of certain members of the chain will disrupt this equilibrium, and some ores are produced where this has occurred. Most are in equilibrium, however, and where this is the case it is possible to estimate rather closely the amount of daughter products present in the ore from knowledge of its uranium content. Each pound of uranium contained in the ore has an alpha activity of 150 microcuries (μc) and, since at equilibrium this is also the activity level of each of the daughter products, the

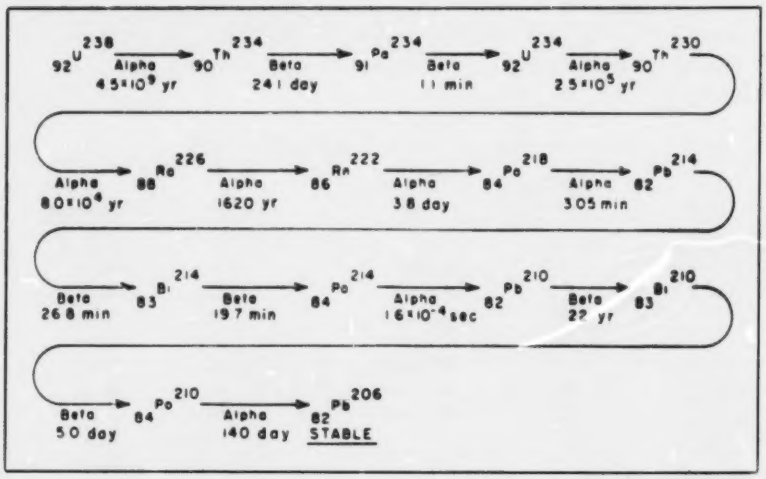

Figure 2. Uranium-radium family - minor branches not shown.

total combined alpha and beta radioactivity of the ore is 2.1 millicuries (mc) per pound of uranium. The total radioactivity of the ore delivered daily to the mills in 1960 may then be estimated at approximately 200 curies, of which 115 curies per day is alpha and 85 curies per day is beta activity. Some 85 percent of this activity, or 170 curies daily, becomes mill waste, the remainder being recovered in the uranium concentrate.[12] It is this large amount of radioactive waste material which presents the major disposal problem of the uranium milling industry.

RADIOACTIVITY IN WASTE

The gross radioactivity of the mill waste material is attributable to each member of the uranium-radium series originally present in the ore. Though milling processes are designed to extract uranium from the ore, some small portion (1 to 10%) of the total uranium remains in the waste liquors and spent ore solids.

The relative degree of hazard presented by each of these isotopes covers a wide range. Table 2 lists each of them in order of increasing maximum permissible concentrations in water, (MPC_W values), or decreasing degree of hazard. The first isotope listed, radium-226, is the most hazardous with an MPC_W of only 3.3 micromicrocuries per liter ($\mu\mu c/l$). It

has, in fact, the lowest MPC_w of any of the 264 isotopes considered by the National Committee on Radiation Protection (13) and the International Commission on Radiological Protection.[14]*

Table 2. URANIUM-RADIUM FAMILY, MPC_w VALUES[a]

Isotope	MPC_w $\mu\mu$/l	Critical organ	Half-life	Emission
Ra^{226}	3.3	Bone	1,620 yr	Alpha
Pb^{210}	33	Kidney	22 yr	Beta
Po^{210}	233	Spleen	140 day	Alpha
Th^{230}	667	Bone	8×10^4 yr	Alpha
Th^{234}	6,667	GI tract	24.1 days	Beta
U^{234}	10,000	GI tract	2.5×10^5 yr	Alpha
U^{238}	13,300	GI tract	4.5×10^9 yr	Alpha
Bi^{210}	13,300	GI tract	5 days	Beta
Pa^{234}	b	-	1.1 min	Beta
Po^{218}	b	-	3.05 min	Alpha
Po^{214}	b	-	1.6×10^{-4} sec	Alpha
Bi^{214}	b	-	19.7 min	Beta
Pb^{214}	b	-	26.8 min	Beta
Rn^{222}	(gas)	Lung	3.8 days	Alpha

[a] MPC_w value is the maximum permissible concentration in water, for average member of the general population (1/30th HB69 value for continuous occupational exposure).[13, 14]

[b] No value given.

The amount of radium-226 contained in the ore produced in 1960 is estimated to be about 5400 curies (or grams). This is more than five times the estimated total United States inventory of purified radium-226 for all medical and industrial uses.[15] By any measure, the amount of radium-226 contained in the ore delivered to uranium mills is very large relative to what are considered safe concentrations. Essentially all of this radium will be contained in the mill wastes, and so major waste control efforts are concerned with this isotope.

The isotope listed second in Table 2, Pb^{210} (Lead-210), is a relatively new addition to the list of hazardous isotopes. It was not listed in Handbook 52 (NCRP)[16], but did appear in the 1960 revision of that document, Handbook 69. Thus, it

* More recently, the Federal Radiation Council has also provided guidance designed to limit radiation exposure of the population.[18] Their recommended exposure limits generally agree with those of ICRP-NCRP. They have as yet considered only four specific individual isotopes.

has received little attention to date as a contaminant in uranium mill waste discharges. A very few reported values [17] for Colorado River waters show Pb^{210} to be present, in one instance, significantly above background levels. The extent to which Pb^{210} may be present in uranium mill waste discharges has not been established, however, and future studies should consider the actual degree of hazard presented by this isotope.

The MPC values climb rapidly as one proceeds down the list shown in Table 2. For this reason, none of the other isotopes listed have been demonstrated to present a significant hazard when radium-226 is also present. For example, some earlier doubt as to the relative hazard of thorium and radium has been resolved[7] with evidence that the hazard due to thorium was near negligible, as compared to the radium-226 present. The uranium MPC's given in Table 2 are based on the chemical toxicity of uranium rather than on its radioactive properties. Such levels of uranium in mill effluents are not normally encountered since they would represent a major economic loss to the industry. It is generally true, therefore, that effective control of radium-226 pollution from uranium mill process wastes precludes any dangerous contamination of receiving waters by the other radioisotopes of the uranium-radium family.

MILL PROCESSES

The process of uranium extraction varies among the mills, this variation being primarily due to the differences in the characteristics of the ores being handled. Process steps which are basic to all mills, however, are crushing, grinding, leaching wherein the uranium is dissolved from the crushed ore, and recovery. The latter step involves the selective removal of the uranium from the leaching solution for preparation of the concentrated product. The variety of actual processes now in use are generally described below.[1-5, 19]

ORE RECEIVING, CRUSHING, AND SAMPLING

Uranium ore is usually transported from the mines to the mill by truck, and at the mill is transferred to hopper bins from which it is fed to the process. The first step is a crushing operation which reduces the ore to a uniform maximum size, generally about 3/4 inch. During the crushing operation a precise repetitive sampling procedure is carried out to obtain a representative sample, usually 0.1 percent (2 pounds per ton), of the incoming ore. This sample is assayed for its uranium (U_3O_8) content and is the basis for payment to the mine. The crushed ore is either stored for later blending or fed directly to the next processing step. Blending is necessary when the raw ore is delivered to the mill from different sources and has significantly different compositions. Adjusting the feeding of these ores stabilizes the input to the mill process, and fewer variations in chemical feed rates and other process control procedures are required.

GRINDING

The crushed ore is conveyed to a ball or rod mill which is usually followed by a spiral classifier, and in some cases a cyclone separator. Water is usually added to the ore as it enters the ball mill to form a slurry, or a recycled mill solution may be added in place of water to form the slurry. The maximum particle size of solids in the effluent slurry from the ball mill will vary depending upon the characteristics of the ore,

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and may be less than 65 mesh. After classifying, the ore solids are in a physical state suitable for dissolution of the uranium by a leaching process. Thickening of these solids may be carried out just prior to leaching by passage through sedimentation tanks. The underflow from these tanks is fed to the leach circuit, thereby reducing the volume of slurry to be handled there.

In the case of carnotite ores which may contain valuable amounts of vanadium, the grinding process may be carried out dry following passage of the fine ore through a rotary dryer to reduce its moisture content. At one such mill[7] dry NaCl (5% of weight or ore) is added after grinding and the ore is then roasted (approximately 1 hour at 1500°F). The purpose of the roasting is to convert insoluble vanadium compounds in the ore to soluble sodium vanadates. The roasted ore is slurried in a quench tank with recycled leach solution and is then delivered to the leach tanks for recovery of vanadium and uranium from the ore solids.

URANIUM EXTRACTION

Uranium is extracted from the ground ore slurry by leaching with sulfuric acid at 21 of the mills listed in Table 2. The leaching circuit generally consists of a series of tanks to which the ground ore slurry and sulfuric acid are added; pH is maintained near 1.0. Agitation is provided and the total leaching time generally exceeds 12 hours. Heating of the leach tank contents is sometimes practiced to speed the dissolution rate of uranium and reduce leaching time. Figure 3 presents a flow diagram of an acid leach mill.

Alkaline carbonate leaching is practiced in six mills where the ore has a high carbonate content (high lime ores) which makes the acid requirements for leaching excessive. A typical carbonate leach circuit consists of a number of tanks or autoclaves in series, each having a detention period of several hours, giving a total leaching period of from 10 to 72 hours. Heat and often pressure are provided to maintain leaching temperatures up to 250°F. If uranium is to be dissolved, it must be in the hexavalent form. The leach tanks are aerated, therefore, to oxidize the reduced uranium present. Copper sulfate and ammonia, or other catalysts, may be added to accelerate the oxidation reaction. An alkaline leach mill flow diagram is shown in Figure 4.

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A

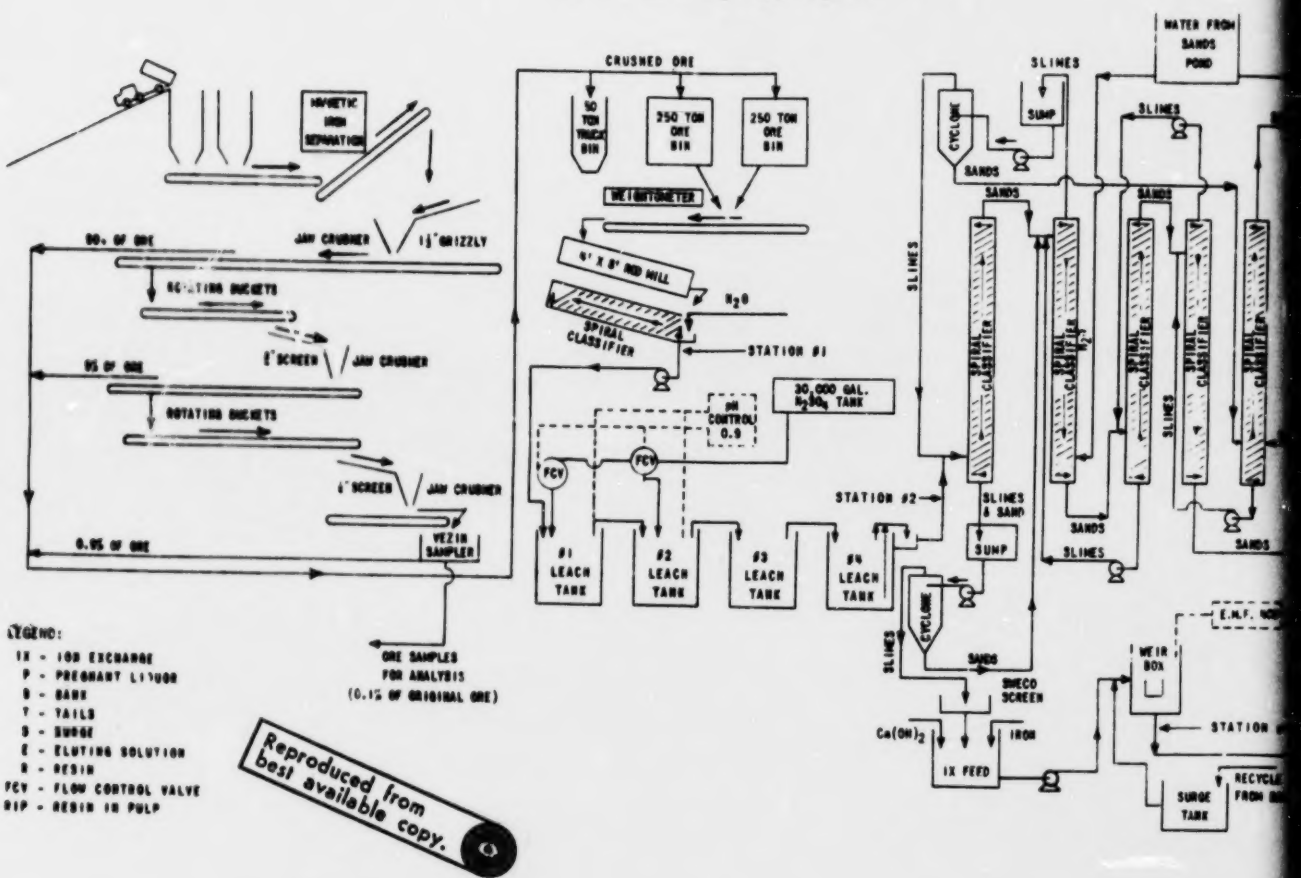
SAMPLING AND CRUSHING

GRINDING AND LEACHING

SANDS-SLIMES SEPARATION

ORE + ACID ⇌ SOLUTION

$UO_3 + 2H_2SO_4 \rightleftharpoons UO_2(SO_4)_2^{=} + H_2O + 2H^+$



LEGEND:

IX - ION EXCHANGE
P - PREGNANT LIQUOR
B - BARE
T - TAILS
S - SLUDGE
E - ELUTING SOLUTION
R - RESIN
FCV - FLOW CONTROL VALVE
RIP - RESIN IN PULP

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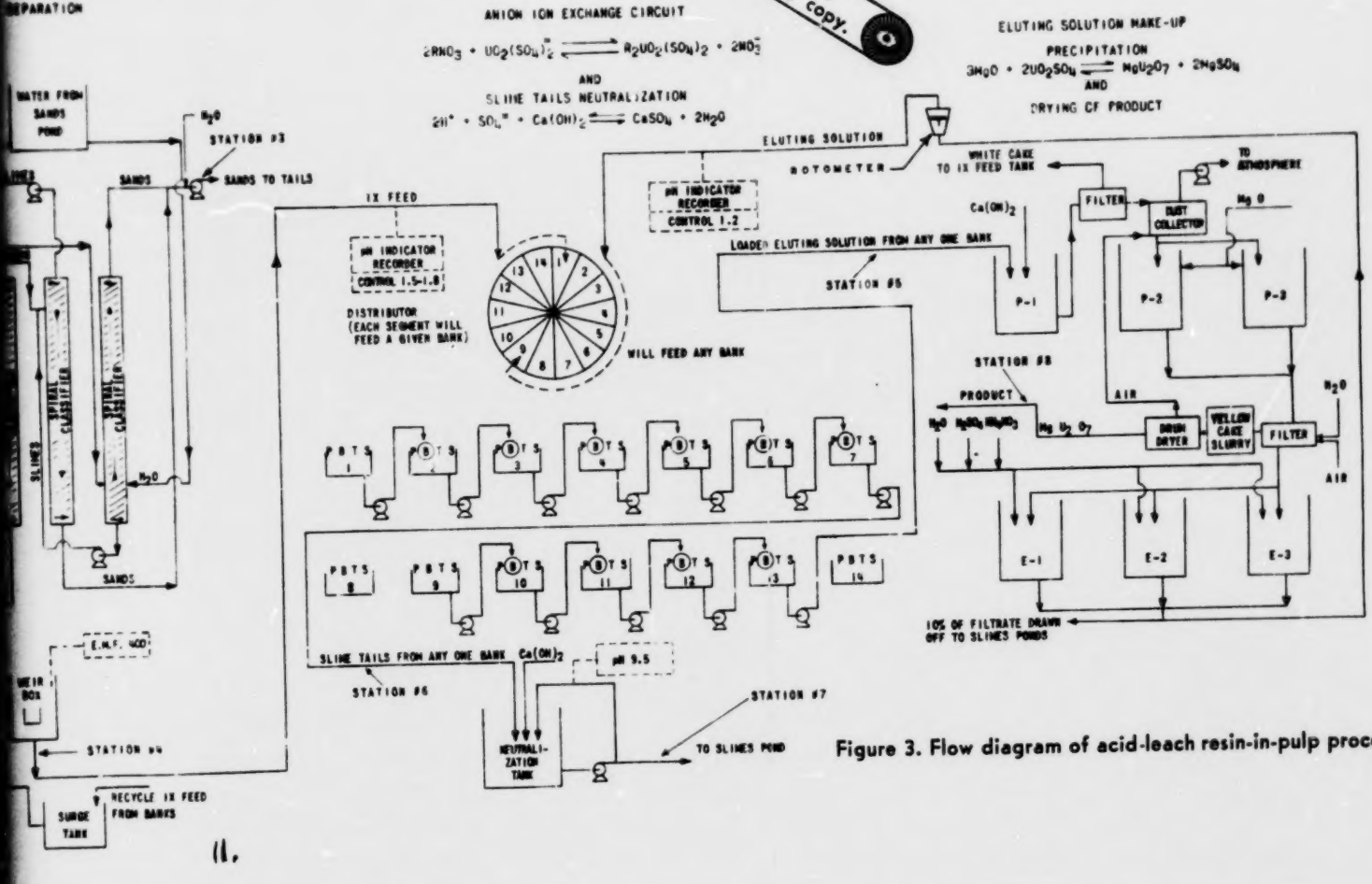

Figure 3. Flow diagram of acid-leach resin-in-pulp process.

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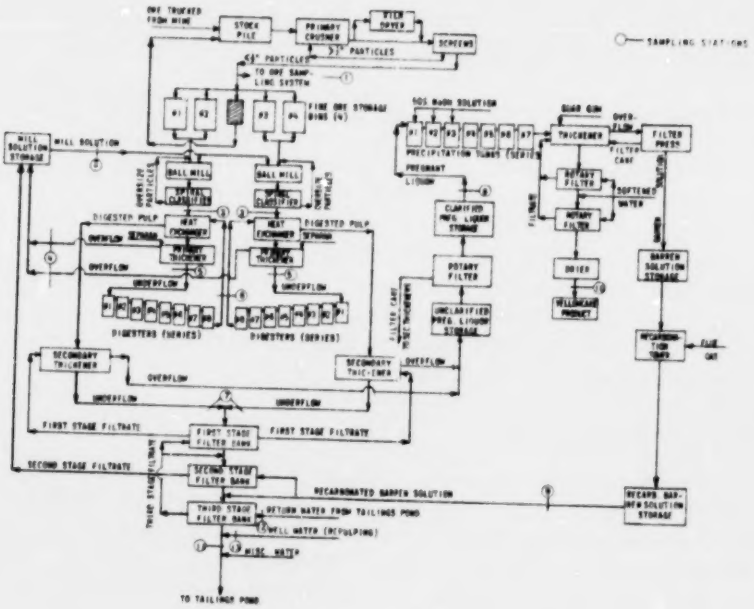

Figure 4. Flow diagram - alkaline leach process.

LIQUID-SOLID SEPARATION

The slurry (or pulp) flow as it leaves the leaching circuit carries the uranium dissolved in the leach liquor as well as a large quantity of spent ore solids, generally about 50 to 65 percent by weight. The first step in the recovery of this dissolved uranium is, therefore, the separation of the spent solids from the liquid. This is accomplished by sand-slime separation, counter current decantation washing in classifiers and thickeners, or filtration.

The separation method used is dependent to a large extent upon whether acid or alkaline leaching is practiced. The alkaline leaches attack the ore solids less severely, and fewer slimes or very fine solid particles are formed. In order to permit recycling of the leach solution and thereby conserve their reagent values, alkaline leaches are processed directly by multiple-stage filtration. Prethickening may be employed, and a synthetic polymer flocculant such as Separan is often used. The resulting filter cake, or "tailings," is a waste material which is discarded. The filtrate, or pregnant liquor,

may be further clarified by aeration-flotation for hydrocarbon removal prior to transfer to the pregnant liquor storage tank.

Since acid leaching results in destruction of the excess acidity, which cannot be regenerated, acid leach pulps are clarified by more economical countercurrent decantation methods (see Figure 3). The sands and slimes are handled separately, the sands being removed by classifiers and the slimes by flocculation and sedimentation in thickeners. Flocculant aids used include gums, glues, starches, and synthetic polymers. The washed sands and slimes are discarded as tailings, and the clarified pregnant liquor is stored for subsequent uranium recovery steps.

URANIUM RECOVERY

Once the uranium content of the ore has been put in soluble form by the leaching process and the unwanted spent ore solids have been removed from the process flow, the next step is recovery of the dissolved uranium. The simplest method is straight chemical precipitation. A relatively clear pregnant liquor containing few dissolved impurities is required. Carbonate leaching dissolves little else from the ore other than the uranium, and as a result direct precipitation may be applied to these leach liquors. Sodium hydroxide is normally used to bring about the precipitation of sodium diuranate at a pH near 12. The precipitated uranium is removed as thickener tank underflow and filtered. This filtrate and the tank overflow are then filtered, and the resulting barren liquor is recarbonated and recycled for use as mill solution in the initial grinding step. This procedure reduces the amount of make-up water and alkalinity required (see Figure 4). The filtered uranium precipitate is heat-dried, ground, and packaged for shipment. This final uranium concentrate is called "yellowcake."

Acid leach liquors contain dissolved impurities which would interfere with the simple chemical precipitation recovery methods. In order to produce a high-grade uranium concentrate product from acid leach liquors, recovery processes utilizing ion-exchange or solvent-extraction principles are used. These processes produce relatively pure and concentrated uranium solutions which are suitable for recovery of uranium by chemical precipitation methods.

Ion Exchange (IX)

Recovery of uranium by ionic-exchange methods (see Figure 3) is a relatively recent development which was found to be advantageous for use in processing ores containing relatively low uranium concentrations. The ion-exchange process has the added advantages of providing a high uranium recovery and a final uranium product of high purity.

The ion-exchange process utilizes the ability of certain anionic resins to selectively adsorb uranium from acid or alkaline leach solutions. When the resin becomes uranium saturated, it is eluted, the uranium being desorbed in a highly concentrated and relatively pure eluate. Alkaline precipitation of this solution removes the uranium and the precipitate, when filtered, yields a high-grade yellowcake.

The principle of ion exchange is applied in practice in two different ways. These are the column-ion-exchange and resin-in-pulp (RIP) processes. In the former process, which is used at three mills, a clarified pregnant liquor solution is passed through fixed beds or solumns packed with the exchange resins. The uranium is adsorbed by the bed resins, and the barren effluent from the exchange unit is recycled for further use or discharged as waste. The RIP process which is used at eight mills, is designed to extract uranium directly from the leach pulp without the necessity for first clarifying the pulp. In this process pulp and resin are contacted countercurrently in a series of tanks. The resin may be confined in screened baskets or it may be fed to the open tanks. In the latter case, shaking screens are used to separate the resin between stages.

After the resins have become saturated with uranium ions, they are eluted with acidified solutions of nitrate or chloride salts. Intricate piping and valving systems are required for the entire cycle of operations, and because of the value of the eluting solutions, it is operated essentially as a closed circuit to minimize losses. In addition, the uranium values of flushing and back-washing waters dictate their conservation by recycling.

Following elution of the uranium from the resins, the eluate is treated with NH_3, MgO, or NaOH to bring about the alkaline precipitation of the dissolved uranium. The insoluble uranium precipitate is recovered and filtered, the filter cake being dried and packaged for shipment as yellowcake. The uranium

recovery procedure for RIP eluates may require an additional step of clarification for slimes removal prior to uranium precipitation. Clarification (usually by lime precipitation) followed by filtration produces a "whitecake" which is repulped and returned to the leach pulp feed to the RIP process.

Solvent Extraction (SX)

Uranium recovery by the solvent extraction process (see Figure 5) is used in 10 Western United States mills. This process employs an organic solvent such as alkylated phosphoric acid or secondary or tertiary amines dispersed in a kerosene diluent which is mixed with clarified leach liquors containing dissolved uranium. The uranium transfers to the solvent, which is stripped of its uranium content when brought in contact with a second aqueous solution which alters the form of uranium so that it preferentially transfers back to the aqueous phase. Stripping agents used include sodium carbonate and acidic chloride or nitrate solutions, the selection of which is dictated by the solvent extractant being used. The stripped or barren solvent is recycled and may be used indefinitely with periodic additions to make up losses. Aqueous raffinate, which is the barren leach liquor, is discarded after the entrained solvent has been scavenged and may be used in pulping waste tailings. Scavenging of the entrained solvent is not complete and some amount of organic solvent leaves the mill in the raffinate waste effluent.

As with ion-exchange eluates, uranium is recovered from solvent extraction strip liquors by chemical precipitation and filtration. The chemicals used in this step are alkaline materials such as MgO, MaOH, or NH_3 which raise the pH to the point where insoluble uranium compounds are formed.

UPGRADING

Four of the plants shown in Figure 1 are classified as concentrators or upgraders. At these plants a wet sand-slime separation of the ground ore is carried out in classifiers. The coarse sands, which constitute much of the ore bulk but contain little of the uranium, may be acid-leached and washed before being discarded. The uranium in the acid liquor is precipitated by neutralization with ammonia. This precipitate, called green sludge, is combined with the unleached slimes and filtered. The resulting filter cake is then dried and shipped

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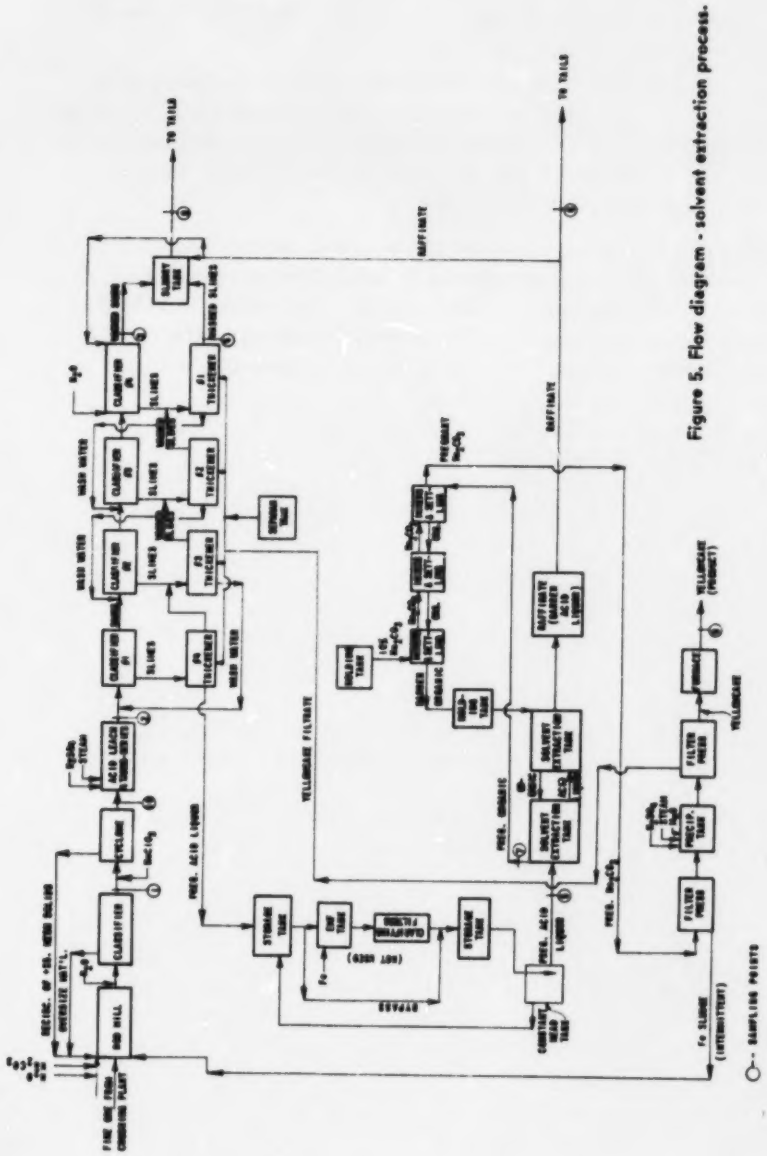


Figure 5. Flow diagram - solvent extraction process.

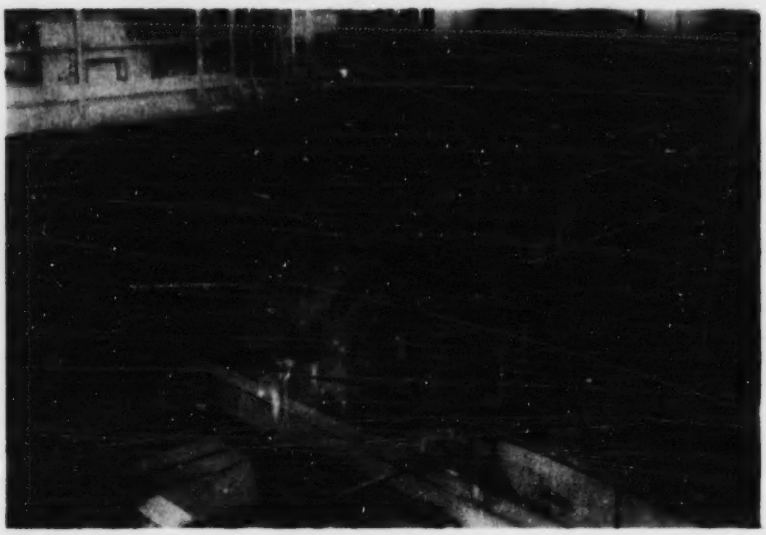
for use as feed material for a complete process mill. The neutralized leach liquor from which the uranium has been precipitated is used in pumping the leached sands to the tailings pile.

The upgrading circuit reduces considerably the bulk of material which must be shipped to the uranium mill. This upgrading process thereby permits the economic development of ore bodies remote from the main mill which otherwise could not be competitively developed.

The foregoing constitutes a general description of the uranium extraction processes in use. For complete details on circuits, equipment, etc., in use, the reader is referred to the detailed process descriptions contained in the reports of individual mills,[1-5] or to a detailed reference work.[19]

Uranium ore being delivered by truck to the mill. The ore is weighed and moisture content determined. (Photograph courtesy of Mines Development, Inc.)

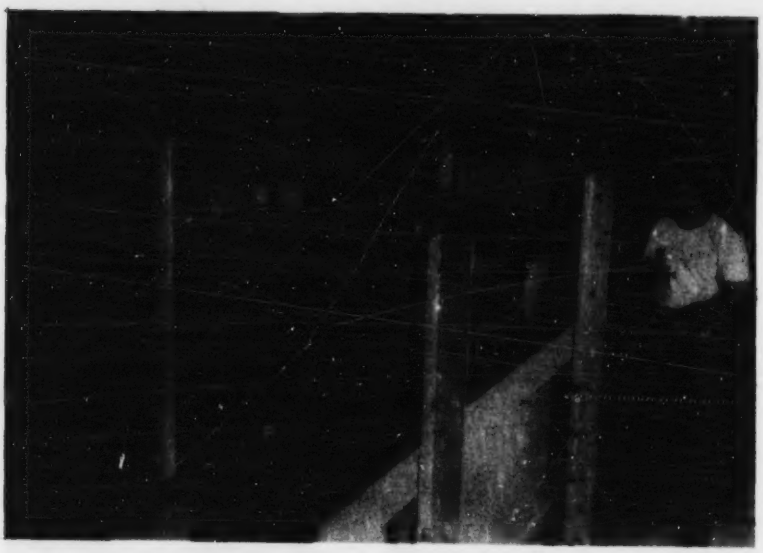
The ore is stored in separate piles according to uranium content. The various grade ores are blended prior to processing in order to stabilize the input to the mill. (Photograph courtesy of Mines development, Inc.)



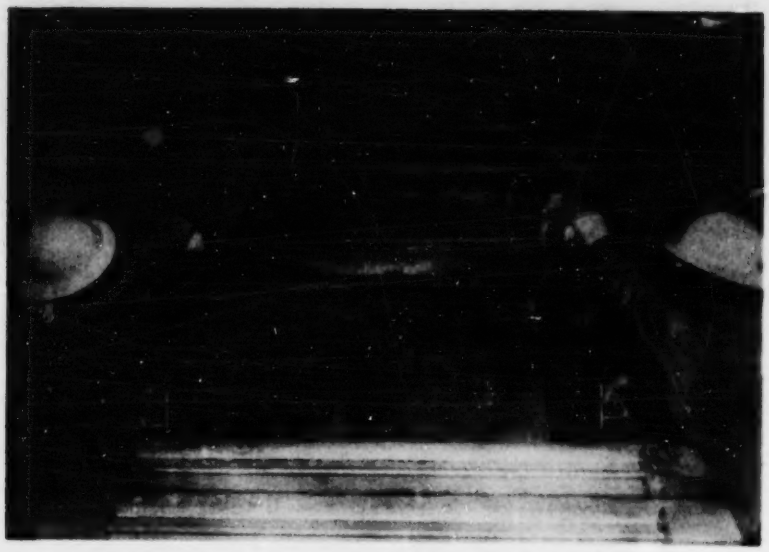
After being crushed the ore is mixed with water or mill solution and ground. A rod mill, as shown above, is often used. (Photograph courtesy of The Anaconda Company)

The ground ore slurry is pumped to these tanks where the uranium is leached from the ore. (Photograph courtesy of The Anaconda Company)

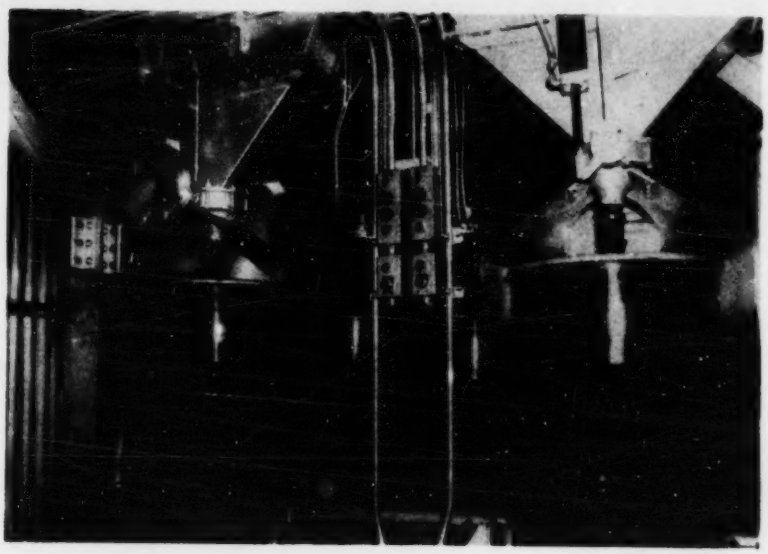
The solids are removed from the leached ore slurry in classifiers. A rake classifier is shown. (Photograph courtesy of The Anaconda Company)



Where the resin-in-pulp process is used, ion-exchange resins contained in metal baskets are used to extract the uranium from the pulp slurry. (Photograph courtesy of Mines Development Company)



The dissolved uranium is precipitated and filtered. A plate and frame filter press is shown. (Photograph courtesy of The Anaconda Co.)



The filtered yellowcake is dried and packaged for shipment in 55-gallon drums. (Photograph courtesy of The Anaconda Company)

PROCESS WASTES

THE MILL BALANCE

The raw materials and the processing procedures previously described, make it clear that numerous opportunities exist for the production of liquid-borne waste materials detrimental to the aquatic environment. To determine the exact quantitative and qualitative nature of the waste flows which can be expected from the various ore refining processes described, extensive field studies were carried out at a number of mills representative of each major type of process. The objective of these studies was to establish a materials balance for each mill, so that the important constituents of the raw ore as well as materials added during processing could be accounted for as the ore passed through the individual processing steps. With the information thus developed, it is possible to characterize the waste streams which could be expected from each method of ore processing. The findings of five such mill studies have already been reported.[1-5]

A balance of materials for the mill processes described is achieved by a combination of field and laboratory data. At the mill, slurry flows are sampled at enough stations to provide an adequate description of the total process. Process flow characteristics should be measured with sufficient frequency that fluctuations arising from batch type operations are incorporated into the data. Representative composite samples of the flow, whether as a slurry or as solids, are necessary. Analysis of these samples provides information on the physical and chemical characteristics of the process stream. Radioactivity analyses are also carried out for determination of radium-226 and gross alpha and beta activity concentrations.

Combining the flow data with the physical characteristics of the process stream permits the calculation of average liquid, dissolved solids, and suspended solids flows passing each sampling station. With careful selection of sampling locations and adequate frequency and duration of sampling, a balanced solids-liquids flow chart for the process can be established with

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Combining the flow data with the physical characteristics of the process stream permits the calculation of average liquid, dissolved solids, and suspended solids flows passing each sampling station. With careful selection of sampling locations and adequate frequency and duration of sampling, a balanced solids-liquids flow chart for the process can be established with

reasonable accuracy. After a liquid solids-flow balance is achieved, the suspended and dissolved radioactivity concentrations can be applied to develop a balance for these materials as well. The net result of these computations should present a clear picture of the changing composition of the process stream as it proceeds through the mill, and a quantitative and qualitative characterization of the waste flows leaving the mill.

The materials balance obtained for an alkaline leach mill[4] illustrates the methods used. At this mill process sampling was conducted during two consecutive sampling cycles of 72 hours each. At 11 of the 14 sampling stations a single representative sample was obtained for each cycle by compositing volumes proportional to the flow every 2 hours for the duration of the cycle. Each composite sample then was made up of 36 portions. Portions of the official mill sample of the raw ore lots were obtained and composited according to the tonnage of each lot processed during the cycle. In a similar manner, composite yellowcake samples representative of the ore processed during each cycle were collected. An automatic sampling device was used to collect a representative sample from the waste slurry discharged to the tailings pond. The mill balance was performed on each cycle, and average values were presented because of the close agreement obtained between cycles.

The results of laboratory analyses, as shown in Table 3, and knowledge of the ore tonnage made possible the calculation of a solids balance across each circuit in the mill process. A schematic process flow diagram is shown in Figure 6. Knowledge of the rate of raw ore feed (and its moisture content) at Station 1, the total weight of collected samples, and analytical information on specific gravities of the slurries and dry solids (Table 3) can be used to calculate solids, liquid, and slurry flows across the ball mill and classifier circuit. This is accomplished by preparing simultaneous equations based on the conservation of material. For example, the slurry flow at Station 3 must be accounted for at Stations 1 and 2. This applies to solids (suspended and dissolved) as well as liquids. Similarly the flows at Stations 4 and 5 should equal that at Station 3. Other circuits within the process are handled in the same manner. The flows shown on Figure 6 are the result of such an analysis. These calculated flows may be checked against

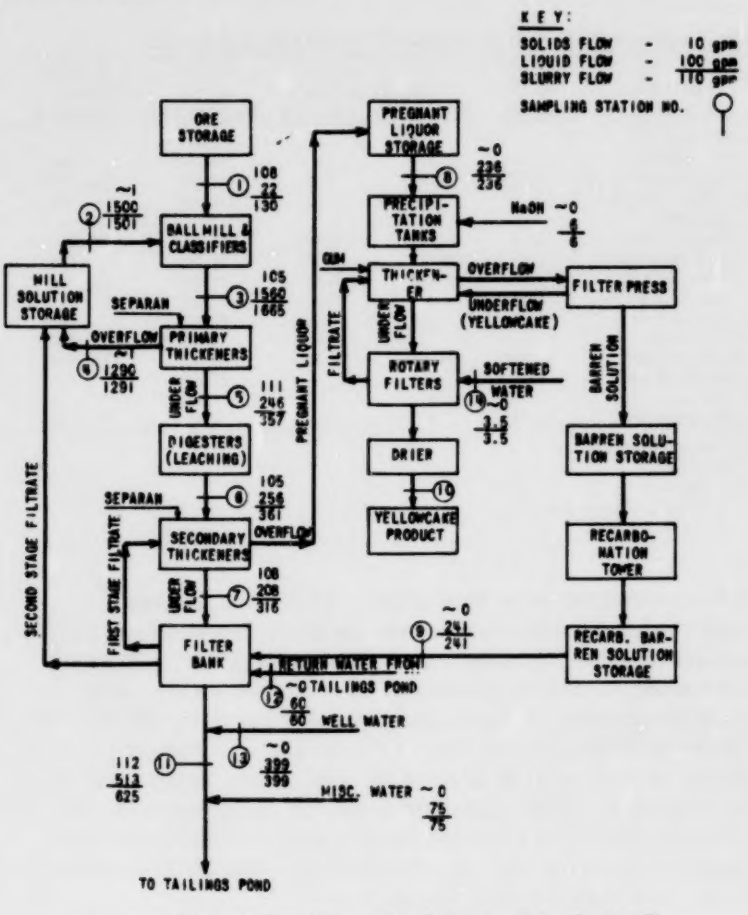

Figure 6. Schematic flow diagram, flow balance - alkaline leach mill.

actual slurry flow measurements made at a number of points in the process.

The slurry flows thus obtained may be used together with the dissolved and suspended solids concentrations (Table 3) to develop a solids balance for the mill as in Figure 7. Here again the solids flow entering a junction point in the process must equal that leaving. For example, the raw ore feed (Station 1) and mill solution (Station 2) have a combined input to the classifier circuit of 2898 (1258 + 1640) tons per day as compared to the output of 2900. This 2900 tons per day is also the input to the primary thickeners whose combined out-

Table 3. PROCESS STREAM CHARACTERISTICS[a] - ALKALINE LEACH MILL[b]

Station	Slurry specific gravity	Dry suspended solids by weight, %	Specific gravity of dry solids	Dissolved solids, mg/l of slurry	Suspended solids (dry weight), %
1 Ore feed	-	-	-	[c]	[c]
2 Mill solution	1.12	[d]	-	138,000	850
3 Classifier overflow	1.19	13.9	2.60	126,000	165,000
4 Primary thickener overflow	1.12	[d]	-	137,000	780
5 Feed to leach	1.50	51.2	2.46	87,900	765,000
6 Leach discharge	1.50	50.2	2.59	94,500	752,000
7 Filter feed	1.56	54.6	2.50	91,300	854,000
8 Pregnant liquor	1.11	[d]	-	159,000	145
9 Barren liquor	1.13	[d]	-	162,000	50
10 Yellowcake	-	-	-	[c]	[c]
11 Repulped tails	1.26[e]	34.6[e]	2.40	12,200	435,000
12 Tails pond water	1.01	[d]	-	14,800	198
13 Well water	1.00	[d]	-	1,880	8
14 Softened water	1.00	[d]	-	1,700	56

[a]Average of Cycles I and II.
[b]Reference 4.
[c]Solid sample.
[d]Liquid sample (negligible solids).
[e]Based on Cycle I only.

put was calculated to be 2896 (1067 + 1829) tons per day. Although the total solids flow across the digesters should remain constant (1829 in, 1824 out), it is apparent that 15 to 20 tons of the entering suspended solids left as dissolved solids. Across the entire process 1669 tons per day enter the mill, 1640 in the raw ore at Station 1, 5.8 tons in return water at Station 12, 5 tons in the well water at Station 13, and 18 tons in the form of caustic soda at the precipitation tanks. This agrees with the calculated total solids leaving the process as waste to the tailings pond (1666 tons per day, Station 11) and in the yellowcake product (2.5 tons per day, Station 10).

Once a satisfactory solids balance has been obtained for the mill process, as in Figure 7, a similar balance can be attempted for the radioactivity contained in the solids. Table 4 shows the radium-226 concentrations in the dissolved and suspended solids, as determined by laboratory analysis, for the alkaline leach mill shown in Figures 6 and 7.

These radium-226 concentrations, as well as the majority of all others mentioned in this report, were determined by the radon emanation technique. The use of this method precludes obtaining radium-226 values which are too high because of the imperfect chemical separation required in other methods. For determination of dissolved radium-226, care was also taken in sample preparation to avoid high results. Separation of sus-

pended solids in the sample was accomplished by filtration through a membrane filter. The necessary sample acidification step was performed after solids separation to avoid the dissolution of radium-bearing particulate matter.

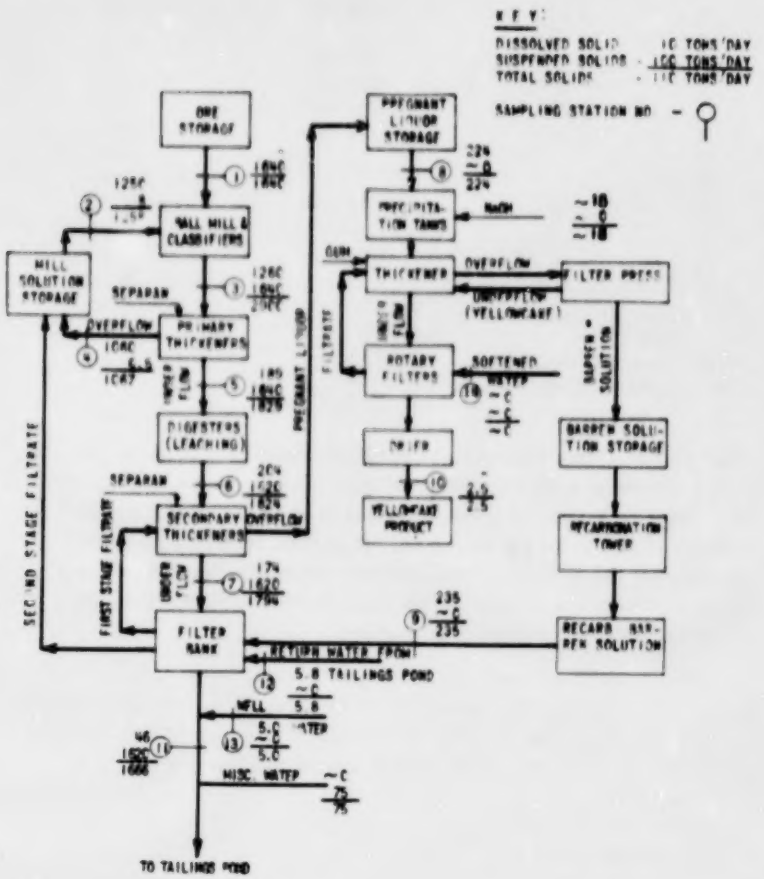

Figure 7. Schematic flow diagram, solids balance - alkaline leach mill.

Applying the concentrations found at each station to the solids flow at that station results in the radium-226 flow diagram shown in Figure 8. Here we see that the 739 milligrams per day of radium-226 entering the process agrees well for this type of balance with the 766 milligrams leaving; 750 in the waste effluent (Station 11) and 16 in the yellowcake product

Table 4. RADIUM-226 CONCENTRATIONS[a] -- ALKALINE LEACH MILL[b]

Station	Radium-226, μμg/l of slurry		Dry suspended solids, μμg/g
	Dissolved	Suspended	
1	-	-	497
2	9,560	1,220	1,440
3	8,300[c]	83,900	508
4	8,790	d	d
5	5,160	328,000	500[c]
6	6,620	370,000	492
7	5,280	380,000	445
8	18,900	286	1,970
9	59	5.4	107
10	-	-	7,190
11	34	222,000	510
12	35	d	d
13	5.4	d	d
14	4.2	d	d

[a]Average of Cycles I and II.
[b]Reference 4.
[c]Most probable concentration.
[d]Not determined (negligible solids).

(Station 10). The balances around individual circuits in the mill process are in equally good agreement. A balance such as in Figure 8 is revealing as regards the fate of the radium content of the entering raw ore. It makes possible an understanding of the portion of the radium which is dissolved from the ore, the point at which this dissolution occurs, and the ultimate fate of the dissolved radium.

The results of such balances performed for mills employing various milling processes have been used in the succeeding sections to describe the flow of radioactivity, primarily radium-226, through the mills and to characterize the various resulting waste flows.

RADIUM-226

Raw ore as it enters the mill process contains 150 micrograms of radium-226 per pound of uranium, if secular equilibrium exists. This radium is entirely in solid or undissolved form. As the ore passes through the various unit operations within the mill, a small portion of the radium is dissolved. This dissolved radium may be partially precipitated to appear in solid form in the yellowcake uranium concentrate, while the remainder of the dissolved radium leaves the mill in the

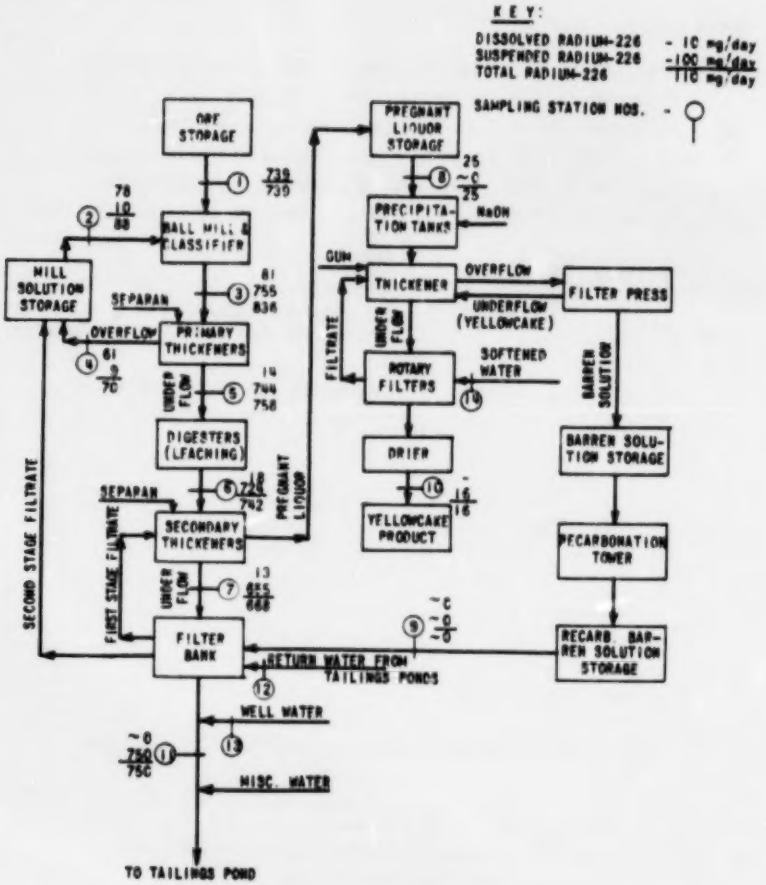

Figure 8. Schematic flow diagram, radium-226 balance - alkaline leach mill.

liquid waste effluents. The radium remaining undissolved during passage through the mill, which comprises all but a small percentage of that entering, can be found in the solid ore tailings which are discarded by the mill as waste. The amount of radium which is dissolved during milling, the percentage precipitated in the concentrate, and the amount to be found in the mill waste streams all vary within a small range depending on the particular milling process being employed.

Acid Leach - RIP[5]

A mill using this process was studied, and the radium balance shown in Figure 9 developed. In this case, of the 300 milligrams of radium entering the mill per day, 2 milligrams (Stations 3 and 4) were dissolved during acid leaching. Of the total radium, 27 percent, including 60 micrograms of the dissolved radium, was discharged to waste

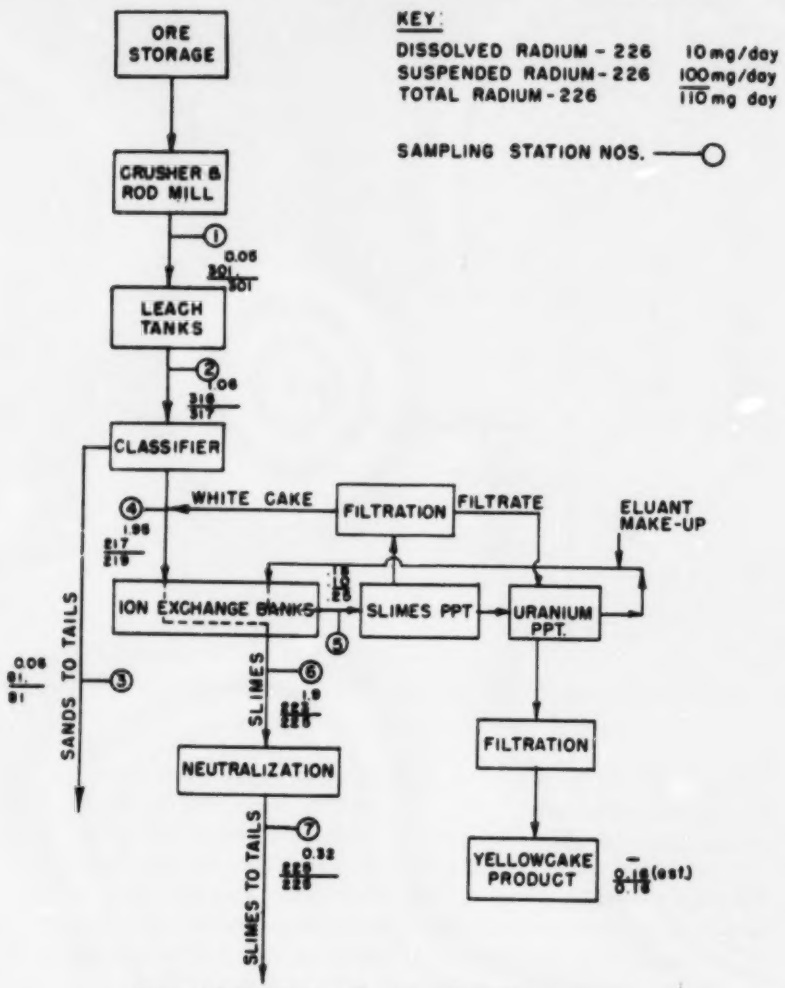

Figure 9. Schematic flow diagram, radium-226 balance - acid leach-RIP mill

with the leached sands. Of the dissolved radium remaining in the process, 150 micrograms was extracted from the slimes along with the uranium and became a part of the uranium concentrate product or yellowcake. The slimes tails leaving the ion-exchange banks contained 1.9 milligrams of dissolved radium and 223 milligrams in an undissolved state. Neutralization of these slimes resulted in the precipitation of a substantial fraction (85%) of the dissolved radium present.

Thus, in this process 0.7 percent of the radium input was dissolved by acid leaching. 0.05 percent appeared in the yellowcake, and the difference, 0.65 percent, left the process in a dissolved state. Neutralization prior to discharge to the slimes tailings pond, however, reduced to 0.12 percent the fraction of radium input leaving the mill in the dissolved state.

Acid Leach - Solvent Extraction[1]

Figure 10 illustrates the radium balance found for a mill using this process. Here 146 milligrams of radium-226 entered the mill per day, and 560 micrograms (sum of Stations 3, 4, and 5) were dissolved in leaching. The waste sands contained 26 milligrams, whereas the wasted slimes carried considerably more radium, or 116 milligrams per day. Of the radium dissolved during leaching, 90 micrograms left the mill with the sands and slimes and the remaining 470 micrograms entered the solvent extraction step. Of this amount, 25 micrograms per day was extracted with the uranium and could be found in the yellowcake. The dissolved radium remaining in the raffinate or barren acid liquor was discharged to the tailings pond.

At this mill, therefore, about 0.38 percent of the radium entering in the ore was dissolved in the acid leach tanks. A very small portion, 0.02 percent of the input, was extracted and precipitated with the uranium and left the mill in the yellowcake. The remaining dissolved radium, 0.36 percent of the input, left the process in waste flows; 0.06 percent and 0.30 percent of the input in the sand-slime wastes and raffinate, respectively. Part of the raffinate was used to repulp the washed sand-slime mixture and as a result it appears that about 90 micrograms of radium was precipitated so that the total dissolved radium discharged to tails was actually only 0.31 percent of the radium input. The bulk of the radium

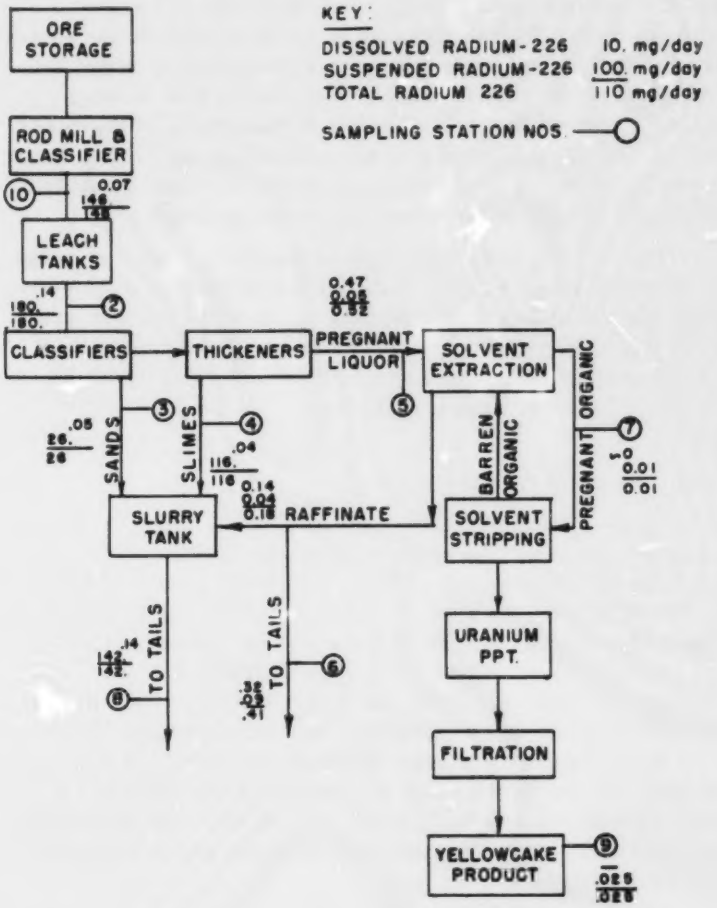

Figure 10. Schematic flow diagram, radium-226 balance - acid leach-SX mill.

input (99.7%) remained undissolved. 18 percent of this contained in the sands and 82 percent in the slimes.

Alkaline Leach[4]

Significantly higher dissolution of radium has been encountered where the alkaline leach process is used. As shown by the radium balance found for such a mill (Figure 8). 739 milligrams of radium-226 per day enters the mill in an undissolved state. The ore enters the ball mill - classifier

GPO 825890-6

circuit, where recycled mill solution containing a high dissolved radium content is added. Radium dissolution begins at this step and continues through the thickening and leaching tanks. The pregnant liquor that overflows from the secondary thickening step following leaching contains about 20 milligrams of dissolved radium per day. All of this radium is precipitated from solution along with the uranium and may be found in the yellowcake. The underflow from the secondary thickeners contained about 13 milligrams of dissolved radium as it entered the filtration circuit. This filtrate which contains the dissolved radium is recycled back into the process, and an essentially dry filter cake is produced. Fresh water and/or return water from the tailings pond is used to repulp this filter cake to form a slurry which is discharged to the tailings pond.

For alkaline leach mills, the, it may be expected that about 2 per cent of the radium-226 input will be dissolved and that essentially all of this will subsequently be found in the uranium concentrate product. The process waste is essentially a dry filter cake containing very small amounts of dissolved radium.

Summary

The alkaline leach process causes greater dissolution of radium from the ore than does acid leaching; however, virtually all of the dissolved raium in the alkaline process leaves the mill in the yellowcake (see Table 5). In contrast, the yellowcake produced by acid mills contains very little radium, about 5 per cent of that dissolved during leaching. That dissolved radium which does not appear in the yellowcake is discharged to the tailings ponds.

Table 5. DISSOLVED RADIUM-226 IN URANIUM MILL PROCESS FLOWS

Process	% of Total Ra dissolved by leaching	% of Dissolved Ra leaving mill	
		in Tailings flow	in Yellowcake
Acid Leach	0.4 - 0.7		
Solvent extraction[a]			
Raffinate		(80)	
Sands and slimes		(15)	
		95	5
Resin-in-pulp[b]		93	7
Alkaline Leach[c]	1.5 - 2.2		100

[a]Reference 1.
[b]Reference 5.
[c]References 3 and 4.

It has been observed that the radium contained in the slimes fraction comprising about a third of the total waste solids represents a large portion (70 to 80%) of the total radium originally present in the ore. Analysis of a tailings sample from an acid leach mill showed that the minus-400-mesh particles have a radium concentration more than seven times that found in the plus-200-mesh particles.[20] At the acid leach mills discussed above, the radium concentration in the slimes particles was three times that in the sands in one case, and 22 times greater in the other. It is clear that the slimes represent the major source of undissolved radium waste from acid leach mills.

Table 5 is a summary of findings pertaining to the content of dissolved radium-226 in process flows. The figures given there may be applied to a particular mill to provide an estimate of dissolved radium discharged as waste. For example, an acid leach - solvent extraction mill processing 1000 tons of "six pound ore" (0.3% U_3O_8) per day would have a radium input of about 765 milligrams per day if secular equilibrium exists in the ore (85% U/U_3O_8 x 6 lb U/ton x 1000 ton/day x 0.150 mg Ra/lb U). About 3 to 5.5 milligrams per day would be dissolved during leaching. 80 percent, or 2.4 to 4.4 milligrams per day, would be discharged in the raffinate, 15 percent or 450 to 800 micrograms per day, with the sands and slimes, and 5 percent or 150 to 300 micrograms per day, could be expected in the yellowcake.

Others have reported[20] radium dissolution during acid leaching up to an order of magnitude higher than the values shown in Table 5. The reason for this lack of agreement is not known. The methods used for radium analyses differed in each case, however, and this may represent a possible source of disagreement. The radon emanation method of radium analysis as used herein is more selective for radium-226 and is recommended for use.

GROSS ALPHA RADIOACTIVITY

At each of the mills discussed previously where a radium balance was obtained through the process, a similar balance was attempted for gross alpha activity. The amount of gross alpha activity entering the mill in the ore can be estimated from knowledge of its uranium content. Uranium-238 is the parent isotope of a long chain of radioisotopes which includes eight

alpha emitters. If no selective leaching has occurred during its geologic history, secular equilibrium can be expected in the ore, viz., the daughter elements are being formed at the same rate at which they are decaying. The activity of each of the eight alpha emitters in the chain, therefore, would be the same. The total alpha actvity then should amount to about eight times the activity associated with a pound of uranium-238, or about 1200 microcuries per pound of uranium-238.

The actual amount of alpha activity detected in a sample of ground ore has generally been found to be somewhat less than the theoretical amount calculated above. This is due in part to the assumption of secular equilibrium, which may not exist because of natural selective leaching of the ore vein. This leaching diminishes the content of one or more of the isotopes in the chain. The effect of this disruption of the decay chain is to lower the gross alpha activity of the uranium ore. In addition, preparing the sample for analysis (involving such steps as grinding and heating) may permit some of the radon-222, a gas, to escape. Unless special steps are taken in the analytical procedure to permit the reformation of radon-222 in the sample, this loss of radon, together with its short-lived daughters, results in an apparent alpha activity somewhat below the amount actually present in the undisturbed ore. The amount of gross alpha activity actually found by analysis in ores as they enter the mill process has varied from 80 to 96 percent of the amount theoretically present at secular equilibrium.[1, 3-5] A good average figure for use is 90 percent. It is probable that the major part of this discrepancy results in most cases from losses of radon-222 and daughters during mining and transport of the ore and that secular equilibrium does usually occur, to quite close approximation, in the undisturbed ore body before mining.

Proceeding into the mill process, Figure 11 illustrates the disposition of the alpha activity as it passes through a typical alkaline leach mill. It will be noted that a balance over the mill has not been achieved in that the gross alpha activity leaving the mill is but three-fourths, approximately, of that entering in the ore. This phenomenon has been observed in all types of mills, as shown in Table 6. At these same mills excellent radium balances were obtained (radium output/input = 100 ± 4%).

This loss of alpha activity within the mill process is attributed primarily to the loss of some portion of the gaseous emit-

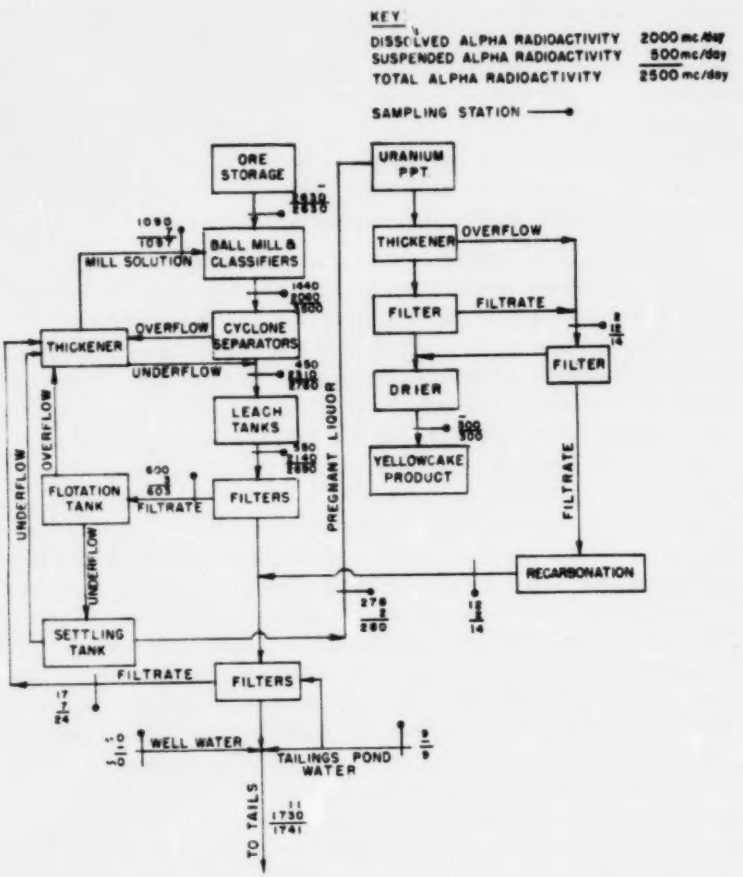

Figure 11. Schematic flow diagram, gross alpha radioactivity - alkaline leach mill.

ter, radon-222, plus the same portion of at least two of its short-lived daughters, polonium-218 and polonium-214, at those points in the process where crushing, grinding, heating, and other ore-handling procedures are carried out. In Figure 11, the observed losses in alpha activity appear to occur primarily during grinding of the ore and in multistage filtration of the spent ore, following alkaline leaching. Approximately 13 percent of the entering gross alpha activity is solubilized when brought into contact with the mill solution in the grinding circuit and an additional 4 percent in the leach tanks. About

Table 6. GROSS ALPHA RADIOACTIVITY IN MILL OUTPUT

Mill process	Reference	Alpha activity as % of observed input		
		Yellowcake	Waste effluent	Total output
Alkaline leach	(3)	11	66	77
Alkaline leach	(4)	15	54	69
Acid leach - SX	(1)	15	65	80
Acid leach - RIP	(5)	14	62	76
Average		14	62	76

[a]Using method of analysis described in Reference 9.

11 percent of the gross alpha input appears in the pregnant liquor, and esssntially all of it is precipitated and can be found in the yellowcake product. The spent sands, which are pumped to the tailings ponds, contain some 66 percent of the gross alpha mill input, and 99.4 percent of this activity is in undissolved form. The percentage of alpha activity in waste streams in dissolved form was found to be higher for both the acid leach - solvent extraction process (2%) and for the acid leach - RIP process (6.5%).

Thus, in general, the total alpha activity of mill wastes is about 3.3 millicuries per ton of ore processed (for a "six pound ore"). A small amount of this activity (0.5 to 6.5%) is in dissolved form, i.e., about 20 to 40 microcuries per ton for alkaline leach mills and 100 to 200 microcuries per ton for acid leach mills.

RADIUM AS PERCENT OF GROSS ALPHA RADIOACTIVITY

The percentage of gross alpha activity in mill samples attributable to radium-226 will usually vary within a small range at a particular location in a given mill, depending upon the source of the sample. It is often useful to establish a general relationship between radium content and gross alpha activity for specific sampling points; this latter analysis can then be used for certain routine monitoring purposes. Since the gross alpha analysis is a considerably simpler procedure, an improvement in process control from the standpoint of radioactive waste disposal can be obtained with little increase in analytical costs.

Table 7 lists radium - gross alpha relationships found in some mills. The range of values found for some types of mill

Table 7. RADIUM AS PERCENT OF GROSS ALPHA ACTIVITY IN MILL SAMPLES

Process	Input	Waste to tailings		Yellowcake	Reference
		Dissolved	Suspended		
Alkaline leach	16	1.8	23	2.1	(3)
Alkaline leach	16	0.4	31	2.3	(4)
Acid leach - RIP	17	3.7	15 (sands)	0.06	(5)
Acid leach - RIP	18	7.1	20 (sands and slimes)	0.07	(6)
Acid leach - SX	11	1.0	31 (sands)	0.01	(1)
		1.3	19 (slimes)		
Acid leach - SX	19	7.0	18 (sands)		
		0.5%	17 (slimes)	0.01	(2)

samples is small; for example, in raw ores where radium accounted for 11 to 19 percent of the gross alpha activity and in alkaline leach yellowcakes where the range was 2.1 to 2.3 percent. Radium in tailings solids was from 15 to 31 percent of the gross alpha, while that dissolved in mill discharges to tails varied from 0.4 to 7.1 percent. The variability of this latter type of sample is dependent to some extent upon whether or not recirculation of tailings pond water is practiced.

Relationships such as those in Table 7 may be established for particular locations in a given mill. So long as no major changes in process or ore sources occur, gross deviations from this relationship will indicate possible errors in analysis.

THORIUM

There are two isotopes of thorium in the uranium-radium decay chain shown in Figure 2. These are thorium-234, which is a beta emitter, and thorium-230, which decays by alpha emission and is the parent of radium-226. In a typical uranium ore which is at secular equilibrium, the activities due to these two isotopes will be approximately equal. According to Table 2 the long-lived alpha emitter, thorium-230, presents an internal human hazard 10 times greater than thorium-234, which has a 24.1-day half-life. Actually the short-lived thorium-234 will decay out following its separation from its parent, uranium-238. For these reasons thorium-230 is the thorium isotope of primary interest in mill wastes.

It has been reported[20] that alkaline leaching does not dissolve any thorium, since its compounds are insoluble at neutral

or higher pH levels. As a result, essentially all of the thorium entering with the ore leaves the mill process in suspended form with the waste tails and only negligible dissolved thorium concentrations can be expected in liquid waste streams for alkaline mills.

It is probable that acid leaching does, however, cause the dissolution of some thorium-230 from the ore.[20] This isotope would then contribute to some extent to the higher dissolved alpha activity of acid leach effluents which were previously noted to contain from two to ten times as much dissolved alpha activity as alkaline leach mill wastes. It is not certain what portion of the dissolved alpha activity is attributable to thorium-230, though concentrations higher than the MPC are possible; however, since this thorium precipitates at a neutral or higher pH, it would not be expected in solution in most natural waters.

URANIUM

Uranium is one of the most toxic elements chemically, although it is absorbed into the body only with difficulty. It is this toxic property rather than its radioactivity which has determined its MPC value. The MPC given for uranium-238 in Table 2, 13,300 micromicrocuries per liter, corresponds to a concentration of 40 milligrams per liter (or ppm).

During leaching, solubilization of over 90 percent of the uranium in the ore is usually achieved. Recovery of this soluble uranium during subsequent processing steps is very efficient, reaching 99 percent in the ion-exchange and solvent-extraction processes. The unrecovered dissolved uranium appears in the mill effluent and amounts to 1 percent or more of that originally present in the ore. Processing a "six pound ore," at the rate of 500 tons per day, for example, would result in a dissolved uranium waste flow of 30 pounds per day or more. At one mill using both alkaline and acid leaching it was found that dissolved uranium losses could have been as much as 160 pounds per day from 514 tons of ore processed daily.[7] In this exceptional case the uranium dissolved in the waste flows was about 7.5 percent of that entering in the ore. Ordinarily, it can be expected that uranium losses will be kept to a minimum since its separation and recovery is the objective of the milling process. Dissolved uranium in waste flows, therefore, will usually be at least 15 to 50 grams per

ton of ore processed, depending upon the grade of the ore and the efficiency of the recovery step.

WASTE SOLIDS

Uranium ore enters the mill process as a solid, and for each ton of ore entering the mill 1 ton of solids, in either dissolved or suspended form, must leave the mill. All of this solid material, except that incorporated in the final uranium concentrate product, leaves the mill as waste.

The extent to which the ore is dissolved during processing varies somewhat with the ore composition. Generally 1 to 3 percent of the ore input is dissolved although even higher values may be encountered. This means that the ore would contribute 20 to 60 pounds of dissolved solids per ton of ore processed to the liquid waste streams. In addition to the dissolved ore solids, the large chemical additions during processing contribute to the final dissolved solids content of the mill waste.

The solids leaving the mill as yellowcake product are but 0.2 percent (four pounds per ton) of the raw ore solids entering the mill. All but a small fraction of the ore solids input, then, can be expected to be discharged as suspended solids or tailings. Since these undissolved solids also contain the bulk of the radium and other radioisotopes originally present in the ore, handling and disposal of the solid waste materials from uranium mills represent a very significant aspect of the total waste disposal problem.

WATER USAGE

As indicated in the various process flow diagrams, fresh water enters the milling process at several points. The amount of water used in the process affects the concentration of waste materials found in the mill effluents and also determines the magnitude of the liquid waste disposal problem to be handled.

The ore as it enters the mill brings with it a small amount of moisture, about 5 percent by weight, or 10 gallons per ton of ore. In wet grinding the ore in the alkaline leach process, recirculated mill solutions are used whereas in acid leach mills fresh water in large amounts is usually added to the process stream at this point. Fresh water may also enter the process in the feeding of reagents, in filter washing, filter cake repulping counter-current washing of sands and slimes in classifiers and thickeners, in flushing and backwashing of ion-exchange columns

where this process is used, and in various other operations. Losses of water from the process are slight, being confined to evaporation from heated leach tanks and from the drying of the yellowcake product. Such losses are of the order of 5 gallons per ton of ore.

The magnitude of liquid waste flows from uranium mills is greatly dependent upon the milling process used and the extent to which solutions are recirculated within the mill. In some cases the amount of water used is partially determined by the availability of water from local sources. Table 8 gives water consumption values encountered in mill surveys. From these data, it is apparent that acid leach mills use considerably greater quantities of water than do alkaline leach mills. It has been reported elsewhere[21] that the alkaline and acid leach processes use 1 and 4 tons of water per ton of ore, respectively, or 240 and 960 gallons per ton. This generally agrees with the figures in Table 8. Even lower water use may be encountered in alkaline mills where waste tails are repulped exclusively

Table 8. LIQUID WASTE VOLUMES

Process	Ore input, tons/day	Net flow to tailings pond, gpm	Net waste volumes, gal/ton	Reference
Alkaline leach	1640	403	354	(4)
Alkaline leach	881	81	132	(3)
Acid leach - RIP	517	193	538	(5)
Acid leach - RIP	2320	1950	1210	(6)
Acid leach - SX	330	219	955	(1)
Acid leach - SX	560	222	572	(2)
Acid leach - SX	515	361	1000	(8)

with recirculated tailings pond waters. In one such case a net water use of 67 gallons per ton of ore has been found.[22]

In general, it would appear that liquid flows to be expected at alkaline leach mills average 250 gallons per ton of ore processed, and may range from 100 to 400 gallons per ton. Acid leach mills produce larger flows, ranging from about 500 to 1200 gallons per ton and averaging about 850 gallons per ton. The higher water consumption for the acid process is due primarily to the procedures used for liquid-solids separation following leaching. Alkaline pulps are filtered directly after

leaching to conserve valuable leaching reagents, which are not irrevocably lost during contact with the ore. In acid processes, however, the sulfuric acid is completely used up during leaching and the barren leach liquor has no further value. In the latter case, the cheaper procedure of countercurrent decantation is employed to separate the spent ore solids from the pregnant liquor. As a result, acid process waste flows are on the average three to four times greater than those from alkaline systems.

As mentioned, some mills recirculate tailings pond water to repulp the separated sands, forming a slurry which may then be transferred to the tailings pond. Water requirements for this purpose are very high. If the slurry formed is 20 percent solids, for example, 4 tons of water is required for each ton of ore, or about 1000 gallons per ton. It can be seen, then, that where tailings water recirculation is not practiced, net waste flows from the mill are greatly increased.

CHEMICAL CHARACTERISTICS

Alkaline Leach Process

In the alkaline leach process a pH slightly above 10.0 is maintained in the leach tanks by the addition of sodium carbonate and bicarbonate to the recycled barren mill solution as needed. Bicarbonate is necessary to prevent the pH from becoming too high and thereby allowing the uranium to precipitate during extraction. Following extraction the spent ore solids are filtered from the pregnant liquor and are discharged as waste to the tailings area. The moisture in the filter cake is highly alkaline and tends to raise the pH of the repulping water.

The pregnant liquor filtrate is treated with caustic soda to achieve a pH of 12, at which point the uranium will precipitate. The resulting barren solution is recarbonated to destroy excess alkalinity, create carbonate and bicarbonate ions, and reduce the solution pH to about 10. While this solution is recycled, a small bleed-off is usually required to prevent build-up of interfering constituents.[23] As a consequence, the pH of waste streams from alkaline process mills is near 10.0 though it may be reduced slightly below that figure by dilution when fresh water is used to transport waste tails.

Another important chemical characteristic of alkaline process waste streams arises from the use of oxidants in the leaching circuit. In natural ores, uranium is found in either the

quadrivalent (uranous) or the hexavalent (uranyl) state. For dissolution of the uranium in the carbonate leach the uranous form must first be oxidized to the uranyl form. This is accomplished by bubbling air through the ore slurry in the presence of catalysts or by adding chemical oxidants. Catalysts most often used with air oxidation are copper sulfate and ammonia. Chemical oxidants include permanganate and cyanide compounds. Table 9 lists reported values of chemical usage for these and other purposes in alkaline mills.

Significant chemical constituents in waste flows are also derived from the raw ore itself. Elements such as boron, selenium, lead, fluorine, and arsenic may be present in some uranium ores, in addition to organic compounds. These materials, if present in the ore, are leached out to some degree during processing and appear in the waste flows. The actual concentrations encountered are specific for each ore

Table 9. CHEMICAL USAGE IN ALKALINE LEACH MILLS[a]

Chemical	Purpose	Usage, lb/ton of ore
$KMnO_4$	Oxidant	7.5
NaCN (and Fe)	Oxidant	0.4
$CuSO_4$	Catalyst	2 - 4
NH_3	Catalyst	3.3 - 6.5
Separan	Flocculant	0.023
Guar gum	Filter aid	0.052
Na_2CO_3	Leaching	2.65
NaOH	Precipitation	17 - 31

[a]References 19, 3, and 4.

and process, however. Table 10 shows waste stream concentrations which have been reported from alkaline mills. These waste analyses reflect the make-up of the particular raw ore being processed and the chemicals added during processing.

Acid Leach Process

The waste streams from these mills differ in composition depending upon chemical usage and the uranium recovery process used, i.e., ion exchange or solvent extraction. All such effluents, however, are highly acidic, since the leaching circuit requires the maintenance of a pH near 1.0 to 1.5. Sulfuric acid is universally employed to provide the needed acidity, and hence, all acid leach liquors can also be expected

Table 10. CHEMICAL CHARACTERISTICS OF MILL EFFLUENTS AS DISCHARGED TO TAILS
(Concentrations in ppm)

	Alkaline leach mills				Acid leach mills						
					Resin-in-pulp				Solvent extraction		
						a	Sands only	Slimes only [a]	Alkyl-amine	EHPA	Amine + TBP [b]
Cl	358	275	286	81	190		240	295	110	235	3740
SO_4	2460	-	-	1760	3860	2210	2180	2330	2910	11,000	7500
Mg	-	-	-	10	535	42	120	75	72		-
NO_3	73	-	-	-	1270	2680	0	2230	-	-	
Cu	.005	-	-	-	1.3	<1.0	-	-	-	0.2	1.6
Be	-	-	-	-	-	-	-	-	-	2.2	0.8
Fe	.52	-	-	0.1	42.	0.1	-	0.14	220	67.	5.4
Mn	< .15	-	-	-	110.	-	7.	-	30	11.	9.1
Pb	-	-	-	-	0.65	0.04	-	-	-	-	
As	< .01	0.20	0.49	-	0.21	<0.01	-	-	-	14.5	4.9
B	-	-	-	-	0.1	0.2	-	-	-	-	-
U	5.6	-	-	-	2.9	0.25	-	-	-	-	34.
Na	-	2950	-	3450	-	910	-	-	-	1055	5400.
Ca	-	-	-	<10	510	815	570	730	520	-	-
HCO_3	-	-	-	1100.	-	-	-	-	-	-	-
CO_3	-	-	-	4610.	-	-	-	-	-	-	-
F	2.0	-	-	-	-	1.2	-	-	3.8	13.	8.0
V		-	-	-	-	-	-	-	-	0.04	34.
TDS	7830	-	-	8270	-	-	-	-	4370	-	19,300
Total alkalinity	1860	4050	3560	-	7360	6410	-	-	-	-	
pH	10.0	9.6	-	10.8	3.3	7.7	-	-	2.6	2.1	2.1-4.1
Reference	(29)	(3)	(4)	(24)	(24)	(24)	(5)	(5)	(24)	(1)	(7) (8)

[a] After neutralization.
[b] Effluents from tails, weighted average.

to have high sulfate concentrations. Other chemicals commonly used in acid leach mills are shown in Table 11.

Table 11. CHEMICAL USAGE IN ACID LEACH MILLS[a]

Chemical	Purpose	Usage, lb/ton of ore
H_2SO_4	Leach	30 - 500
Fe (powder)	emf adjustment	variable
MnO_2	Oxidant	3 - 10
$NaClO_3$	Oxidant	1 - 3
MgO	U ppt (pH adj)	1 - 3
NH_3	U ppt (pH adj)	1 - 30
NaOH	U ppt (pH adj)	1 - 4
EHPA, Alkyl-mine and others	Solvent extraction	0.01-2.0
Kerosene	Solvent diluent	3.4
NH_4NO_3	Solvent stripping	1.3
Na_2CO_3	Solvent stripping	10-15
NaCl	Solvent stripping	10-15
NH_4NO_3	IX-eluant	15-20
NaCl	IX-eluant	7
NaCl	Roasting (vanadium ores)	50-160

[a] References 1, 5, 8, 10, 24, 25, and 26.

Ion-Exchange Recovery

Following acid leaching, the sands and slimes are removed from the pregnant liquor and discarded as waste. In

the case of the resin-in-pulp process only the sands are wasted at this point. Powdered iron may then be added for emf adjustment if ferric iron (Fe_3) or vanadium (V_5) is present in the leach solution. Vanadium in its oxidized pentavalent state adsorbs on the resin but is not eluted, resulting in a poisoning of the resin. By proper adjustment of potential, the vanadium can be maintained in quadravalent form.

The pregnant liquor (containing the slimes in the case of the RIP process) then enters the anionic ion-exchange circuit where one of the following reactions takes place, depending upon whether chloride or nitrate is used in the elution cycle:

$$4RNO_3 + \left[UO_2(SO_4)_3\right]^{-4} \rightleftharpoons R_4UO_2(SO_4)_3 + 4NO_3^-$$

or

$$4\,RC1 + \left[UO_2(SO_4)_3\right]^{-4} \rightleftharpoons R_4UO_2(SO_4)_3 + 4Cl^-$$

These reactions indicate that each uranium disulfate anion removed from the pregnant solution is replaced by two nitrate or chloride anions. As a result the barren liquor slimes stream, as discharged to waste, contains a high concentration of one or the other of these ions, depending upon which is used for resin regeneration.

After the uranium-bearing resin is eluted with an acidic nitrate (or chloride) solution, magnesium oxide, sodium hydroxide, or ammonia are added to the pregnant eluate, producing an insoluble uranium precipitate. This precipitate is filtered out to produce yellowcake, and the filtrate is adjusted with acid and nitrate (or chloride) to make fresh eluant. Thus, elution is a recirculating circuit. The only waste produced is a bleed-off, which is necessary to prevent a build-up of sulfate ions. This waste flow, on the order of 3.5 gallons per ton of ore,[5] has a near neutral pH and contains relatively high dissolved values of magnesium (or sodium or ammonia), nitrate (or chloride), calcium, and other mineral salts.

Table 10 shows the chemical character of waste which can be expected from a resin-in-pulp uranium mill. This effluent reflects the use of a nitrate elution cycle rather than a chloride cycle.

Solvent Extraction Recovery

Wastes from acid leach mills using the solvent extraction process for uranium recovery have chemical characteristics somewhat different from the wastes from mills using ion-exchange methods. Following liquid-solids separation, the pregnant acid liquor enters the solvent extraction tanks where it is mixed with an organic solvent which preferentially picks up the dissolved uranium from the aqueous phase. The loaded solvent and barren acid liquor, or raffinate, are gravity separated, and the raffinate is discharged to waste. The loaded solvent may be stripped of its uranium content by an Na_2CO_3 (or acidified chloride or nitrate) solution; the barren organic is recirculated for reuse; and the loaded stripping solution is treated with sulfuric acid and MgO or NH_3 for uranium recovery.

Although the solvent is entirely recirculated some losses to the raffinate do take place. These are estimated to be usually no greater than 1 to 2 pounds of solvent per ton of ore treated. This amount may then be expected in the raffinate waste stream and a combined mill effluent concentration of about 150 to 330 ppm would result.[24] The solvents primarily used include di-2ethylhexyl-phosphoric acid (EHPA) and alkylamines, with kerosene commonly used as a diluent for the solvents. Tributyl phosphate (TBP) is sometimes added in minor amounts as a supplement to improve the solvent characteristics. The use of Na_2CO_3 and H_2SO_4 during uranium recovery results in high concentrations of sodium and sulfate ions in the raffinate waste stream. Table 10 shows the reported concentration ranges of these and other important chemical constituents of wastes from acid leach - solvent extraction mills. Reported chemical usage is shown in Table 11.

POLLUTIONAL EFFECTS OF WASTES

The liquid wastes produced in uranium milling operations capable of producing significant adverse effects upon receiving stream waters if they are discharged without adequate treatment. The radioactivity in the waste sands and slimes and that dissolved in the waste streams are of greatest significance. In addition, the chemical characteristics of these untreated waste flows are such that, where adequate dilution by receiving streams cannot be provided, direct toxic effects on the aquatic biota and interference with the usefulness of the receiving water as a municipal or agricultural supply can result.

RADIOLOGICAL POLLUTANTS

In order to properly evaluate actual or potential radiological contamination of the environment by uranium mill wastes, it is necessary to consider appropriate radiation protection criteria, which have been developed to assist in controlling human exposure. These criteria or standards have been promulgated primarily by three organizations: the International Commission on Radiological Protection (ICRP), the National Committee on Radiation (NCRP), and most recently, the Federal Radiation Council (FRC). Publications of these organizations[13, 14, 18] give limiting standards for human exposure to all man-made sources of radiation. The primary standards are in terms of radiation dose rate and are essentially the same for all three organizations. Although they set permissible or acceptable levels of human exposure, each of these groups stresses the importance of minimizing to the greatest feasible extent the radiation dose received by the public, and urges that the actual radiation dose be kept as far below the permissible levels as possible.

Direct measurement of the human dose resulting from ingestion of radioactive materials is not possible. This dose can

be computed, however, if the amount and distribution of radioactive materials in the body are known. The limiting dose, therefore, leads directly to a limiting "body burden" or amount of radioactive material retained in the body. Knowledge of rate of biological accumulation and elimination of a particular isotope by the body permits the further calculation of a limiting intake of radioactive material which corresponds to a limiting exposure. For practical control measures, the maximum permissible intake of radioisotopes is the parameter of greatest usefulness. For convenience, these maximum permissible intake levels have been converted to permissible concentrations in drinking water (or MPC_w values) by dividing the intake level by 2.2 liters per day, the amount of water consumed by the "standard" man. By these procedures the ICRP and NCRP have selected MPC_w values for over 250 radioisotopes. These values are applicable to radiation workers and must be reduced by appropriate factors in order to protect the general public adequately. The MPC_w values for members of the uranium-radium family shown in Table 2 are those given by ICRP and NCRP. They are derived from occupational limits which must be reduced by a factor of 30 for application to the average member of the general public.

To evaluate radiation exposure of the public due to radioactive waste discharges completely and adequately, it is necessary to determine the total radioisotope intake from all sources, which may include several environmental media, i.e., food, milk, water, and air. It is useful, however, to utilize the MPC in water values as shown in Table 2, for a general assessment of the degree of contamination of receiving waters resulting from waste discharges.

Radium

Radium-226, with the lowest MPC of all radioisotopes, is the radiological contaminant of greatest concern in uranium mill waste discharges. From the data in Table 5 it can be estimated that for a typical ore approximately 3 to 5 micrograms of dissolved radium will be found in acid leach mill wastes for each ton of ore processed. In order not to exceed the MPC for radium in the receiving stream, the untreated waste discharge from a 1000 ton per day mill of this type, for example, would have to be diluted by a corresponding receiving stream flow of about 400 to 600 cfs.

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A potentially more important waste component is the radium which remains undissolved through the mill process. The suspended radium which is contained in the waste ore tailings represents all but 1 or 2 percent of the radium originally present in the ore. If tailings are permitted to enter the stream, these solids will be deposited and will accumulate for long periods on the stream bed within a short distance from the discharge point. The undissolved radium will be leached from these solids to the overlying waters, increasing the dissolved radium content of the stream. This has been observed to result, in one instance,[27] in a dissolved radium content downstream from a uranium mill of 12 micromicrocuries per liter - about four times the MPC, and more than 20 times higher than would be expected on the basis of the dissolved radium discharged by the mill to the stream. A brief series of laboratory experiments on the leachability of radium-bearing river muds obtained from a stream bed below another mill indicated that from 0.1 to 1.0 percent of the radium in such mud may be leached out with only brief mixing.[7] The actual degree to which radium will leach out of stream bed muds depends upon the stream velocity, degree of turbulence, and bottom agitation.

Detailed laboratory studies have been conducted on the leaching of radium-226 from uranium mill waste solids and river sediments.[36] The mill solids most thoroughly studied were sand and slime mixtures from mills utilizing the acid - leach solvent extraction process for uranium recovery. These solids and the river sediments studied were collected from representative locations in the Colorado Plateau area of the United States. The leaching agents used on these solids were distilled water, various inorganic reagents, and natural river waters.

These studies showed that the most important single parameter affecting the leaching of radium was the liquid-to-solid ration (ml/g). The liquid-to-solid ratios studied ranged from 10:1 to 10,000:1; the amount of radium leached from sands and slime mixtures ranged from 0.10 to between 40 and 50 percent of the total radium associated with the solids. The effect of liquid-to-solid ratio was greater on acid leach waste solids than on river sediments and greater on acid leach waste solids than on alkaline leach waste solids.

The studies also showed that time was not an important factor in the amount of radium leached, an equilibrium amount being leached in about 10 to 15 minutes. Natural river waters leached no greater amount of radium than distilled water, and of the inorganic ions Na^+, K^+, Mg^{++}, Ca^{++}, Sr^{++}, and Ra^{++} only barium exerted a significant effect on radium leachability.

The hydrology of western streams strongly affects the pattern of accumulation of radium-bearing solids on the stream bed. These streams are typically unregulated, and most of the total annual flow occurs within a short period of 2 or 3 months during late spring. Many of these streams run dry or nearly so in the late summer and fall months. Discharged radium-bearing solids build up during such periods of low flow only to be scoured from the point where they were originally deposited by the high flows the following spring. This flushing action can effectively cleanse a badly silted stream below a uranium mill, but the solids which are removed are merely transferred to a downstream location and eventually come to rest in the major reservoirs of the river system. Recent examination of the muds in Lake Mead, on whose tributaries are many of the country's uranium mills, has shown them to have a radium content four times as high as the natural, or background, levels.[28] These findings may be used, together with estimates of the volume of Lake Mead sediments involved, to arrive at a rough estimate of the total amount of radium-226 added to this impoundment by uranium milling operations over the last 20 years. Such calculations, together with a parallel computation based upon ore tonnage processed, earlier practices regarding discharge of waste tails, etc., indicate that some 2500 curies of radium-226 has accumulated in the sediments of Lake Mead since 1940. In the case of a long-lasting contaminant such as radium-226, with its half-life of 1620 years, such an accumulation is highly undesirable and dictates that the spent ore solids be retained indefinitely at their source as is presently the practice.

Where the stream in question is used as a source of municipal water supply, suspended radium-bearing solids may be bound in the filter sand beds of the water treatment plant. They remain there even after backwashing of the filters to slowly release radium into the treated water supply. These effects have been demonstrated in studies of the pollution of the Animas River.[27]

It can be concluded from the above that undissolved ore tailings, if released from uranium mills to streams, represent a highly significant source of very long-term contamination of receiving waters.

If the receiving stream is used as a source of municipal water supply, its dissolved radium content, of course, cannot be allowed to exceed generally recognized standards and should be kept as far below this level as possible. If, in addition, the stream water is used as irrigation water, consideration must be given to possible radium contamination of crops which are raised for human consumption. Radium ingestion via contaminated crops must be included in estimating total intake by the general public in such cases. Studies on the Animas River, a tributary of the Colorado, showed an average radium content for edible crops from irrigated farms below a uranium mill to be about double that of foods from farms above the mill.[7] If cattle feed is grown on irrigated lands, it is possible that significant concentrations of radium may be found in both meat and milk.

In streams receiving radioactive wastes, an uptake of the activity by aquatic organisms can generally be observed. These organisms provide a good indication of past contamination, since they retain the activity taken up during prior periods. Fish, being highly mobile, present a relatively erratic pattern of contamination. Attached algae and aquatic insects, on the other hand, reflect contamination history at a specific place and, therefore, provide a good picture of past contamination longitudinally along the stream.

During a uranium mill survey, samples of attached filamentous algae, bottom dwelling aquatic insects, and fish were collected and analyzed for gross radioactivity and radium content. An analysis of these data[30] indicates that the radium content of either the attached algae or the aquatic insects reflects fairly well the dissolved radium content of the stream. Because of this fact the more easily collected algae should be useful as an indicator of radium-226 pollution. This relationship is shown in Figure 12. The natural radium content of attached algae was found to range from 2.0 to 10 micromicrograms per gram of ashed weight, averaging 4.5 micromicrograms per gram. The average natural dissolved radium content of the associated flowing water was 0.35 micromicrogram per liter. In radium-polluted waters the algal radium content was found to be much

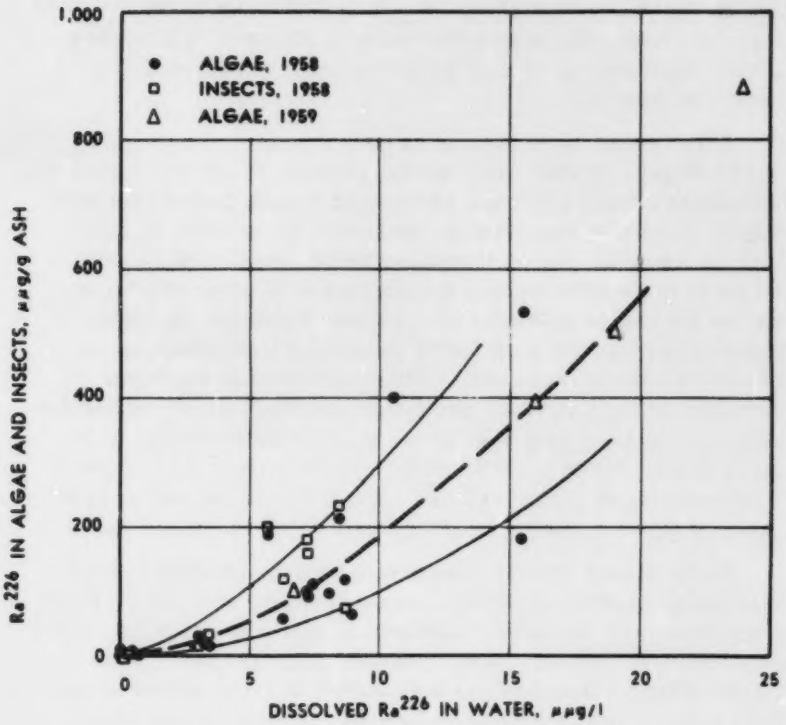

Figure 12. Radium-226 content of algae and insects versus that of water - Animas river.

higher. From Figure 12 it can be seen that, with a dissolved radium concentration of 15 micromicrocuries per liter in the stream, for example, the insect and algal concentration could be expected to lie in the range from 200 to 500 micromicrograms per gram. This uptake of radioactivity by aquatic organisms, which serve as food for edible fish and shellfish, provides another mode of entry for human intake of radioactive materials which must be considered in evaluating total intake.

CHEMICAL POLLUTANTS

Effects on Stream Biota

The Animas River, receiving wastes from a 500-ton-per-day mill using a combination alkaline leach and acid leach -

solvent extraction process with vanadium recovery was studied extensively in this regard.[7] A census of bottom-dwelling organisms above and below the mill discharge was conducted on this stream which, at the time, had a flow of 300 cfs, about 50 percent higher than its annual average minimum 30-day flow. Below the mill virtually complete elimination of bottom-dwelling aquatic insects was observed. Partial recovery was indicated at a station 36 miles below the mill, where the number of species of organisms present increased. However, the total bottom fauna population did not approach normal proportions until the river had flowed for some 45 miles after receiving the mill discharge. Fish populations and types were greatly reduced in these reaches.

In conjuction with these stream investigations, bio-assay studies were performed on the various mill effluents. These tests, in which local fish species are placed in various mixtures of waste effluent and unpolluted stream water, are designed to measure waste toxicity in terms of the amount of dilution required to prevent deaths in the local fish population. Specifically, a median tolerance limit (TL_m) is determined, i.e., that waste concentration at which 50 percent of the test fish will survive a specified exposure period, usually 72 or 96 hours. To permit all of the fish to survive indefinitely, a concentration much lower than the TL_m must be maintained in the receiving stream. The TL_m is, therefore, reduced by an "application factor," which may range from 3 to 10, depending upon the fish food organisms to be protected, variability of the waste, temperature, pH, and chemical characteristics of the river water.

The TL_m values observed for the waste effluents from this acid leach - solvent extraction mill are shown in Table 12. At the minimal application factor of 3, a stream flow of 600 cfs would be required to protect the fishery resources of the stream. From these data it is apparent that at the normally expected annual minimum 30-day stream flow of 200 cfs large numbers of fish would die. On the basis of the mill processing rate of 500 tons per day, the required receiving stream flow for this particular stream would be from at least 1.2 to as much as 4 cfs per ton of ore processed per day by the acid leach - solvent extraction process, depending upon the application factor selected.

Table 12. BIOLOGICAL TOXICITY OF EFFLUENTS DISCHARGED TO THE ANIMAS RIVER - 1958[a]

Waste stream	TL_m range, %	Equivalent dilution flow,[b] cfs
(a) Final tailings effluent	1.3 to 3.3	6 - 16
(b) Primary tails overflow	13 to 18	<1
(c) Vanadium filter tray wash	0.82 to 4.2	2.6 - 14
(d) Raffinate	0.09 to 0.21	34 - 79
(e) Composite sample of (b), (c), and (d)	0.31 to 7.6	7 - 193

[a]Reference 7.
[b]Based upon waste flow discharged.

Subsequent changes in waste treatment and disposal carried out by the mill reduced considerably the amount of suspended solids and organic waste which entered the stream.[8] These modifications resulted in marked improvements in the variety of aquatic biota found in the stream below the mill.

The most toxic single waste noted in Table 12 is the organic-bearing raffinate which had a TL_m of one-tenth the next most toxic waste. For mills using a uranium recovery process other than solvent extraction, the over-all waste toxicity and the resulting dilution stream flow requirement would undoubtedly be considerably less than those discussed above. Because of the variation in chemical content of streams and the importance of this factor of waste toxicity, generalization in this regard is not appropriate and each stream that receives a mill waste discharge must be evaluated as an individual case. Such evaluations have been conducted at a number of mills,[28] and Table 13 summarizes the results of these studies.

Table 13. URANIUM MILL EFFLUENT BIOASSAYS[a]

Mill location	Waste stream	TL_m, %
Moab, Utah	Tailings pond effluent	32 - 42
Rifle, Colorado	Vanadium plant waste	2.4
	Organic-bearing raffinate	0.25
Mexican Hat, Utah	Organic-bearing raffinate	0.20 - 0.39
Slick Rock, Colo.	Waste tails	1.5 - 2.4
Uravan, Colorado	Tailings seepage and ground water	100
	Uranium-Vanadium effluent	0.42 - 0.75
	Redcake (Vanadium) tails	4.2 - 8.0
	Yellowcake filter pond	2.4
Shiprock, New Mexico	Organic-bearing raffinate	0.41

[a]Reference 28.

It is apparent from these results also that the organic-bearing raffinate is the mill waste component most toxic to fish. The TL_m value of this raffinate varied between 0.2 to 0.75 percent meaning that these wastes, if discharged to a stream, would require a minimum dilution factor of 400 to 1500 ($1/TL_m x3$) in the stream. Wastes from vanadium processing circuits exhibited about one-tenth the toxicity of the organic-bearing raffinate.

Effects on Water Uses

A comparison of the chemical content of untreated or neutralized mill effluents (Table 10) with commonly used drinking water standards,[31] as shown in Talbe 14, indicates that several chemical components of the waste are present in relatively high concentrations.

Table 14. DILUTION REQUIREMENTS FOR CHEMICAL POLLUTANTS

Chemical constituent	Limiting concentration,[a] mg/l.	Basis for limit[b]	Ratio of required stream flow to waste flow[c]
Arsenic	0.01	P	1450
Barium	1.0	P	-
Carbon chloroform extract	0.2	A	-
Chloride	250	A	15
Chromium (+6)	0.05	P	-
Copper	1.0	A	1.6
Cyanide	0.01	P	-
Fluoride[d]	2.0	P	4.0
Iron	0.3	A	734
Lead	0.05	P	13
Manganese	0.05	A	2200
Nitrate	45.0	P	60
Sulfate	250	A	45
Total dissolved solids	500	A	39
Uranium[e]	40	P	0.9

[a]Public Health Service Drinking Water Standards, 1961 (Reference 31).
[b]P = Physiological effects; A = Aesthetic considerations.
[c]Using maximum waste concentrations in Table 10; assumes concentration in dilution flow is zero.
[d]Varies from 1.4 to 2.4, depending upon average air temperature.
[e]ICRP-NCRP Standard.

The last column of Table 14 shows the ratio of diluting stream flow to waste flow required to assure that the particular chemical pollutant concentration will not exceed its limiting con-

centration in the receiving stream. The pollutant concentration used in these calculations was the highest value reported in Table 10. Thus, all of these ratios do not apply to a single mill effluent, although one or more apply depending upon the process used.

It is clear that manganese can be a major waste problem wherever it is used as an oxidant in the mill process if liquid wastes are released to a stream. The dilution ratio shown in Table 14 for manganese indicates that for a particular acid mill waste a ratio of receiving stream flow to waste flow of 2200, or about 3000 cfs for a 1000-ton-per-day mill, would be required if neutralization were not practiced. Such a dependable flow is far in excess of that available at most mill sites. A ratio of stream flow to waste flow of 1450 would be required to dilute wastes from the SX mill of Table 10 to prevent excessive arsenic concentrations in the receiving stream, if wastes from that mill were released to the river. (In practice, they are confined in the tailings pond.) This element originates in certain uranium ores, and it is a potential problem only at mills using such ores. Iron dissolved from the ore or abraded from the grinding equipment, or metallic iron used for emf adjustment will be found in unneutralized acid mill effluents, which require a high dilution stream flow. However, simple neutralization of the waste reduces the soluble iron content to negligible proportions, as Table 10 shows.

In mills using nitrate elution of ion-exchange resins, nitrates can be expected in relatively high concentrations in waste streams. Where nitrate compounds are used for solvent stripping, somewhat lower, though still significant, concentrations of nitrate are produced.

Of the potential chemical contaminants listed in Table 14 the more serious involve those which are capable of causing physiological damage to persons using the receiving stream for drinking water. These include elements such as arsenic, barium, chromium, fluorine, and lead which may be contained in raw ores. Compounds containing cyanide and nitrate used in ore processing may be found in waste streams in significant concentrations. The limiting uranium concentration usually is not approached in waste flows, except possibly in some alkaline mills where both water usage and uranium recovery efficiencies are lower than those normally found.

The remaining contaminants listed are objectional primarily for aesthetic reasons: taste, odor, or appearance. Some mill effluents contain excessive amounts of the hardness-producing cations, calcium, and magnesium. The hardness concentration of one mill effluent following lime neutralization was computed to be near 4000 ppm (as $CaCO_3$). Drinking waters with hardness levels exceeding about 250 ppm are usually considered "very hard" and undesirable for domestic use. Certain mill effluent constituents, such as sodium, boron, chlorides, and total dissolved solids, could cause degradation in the stream's value for irrigation use.

Discussion of the pollutional effects of mill effluents on the aquatic environment has been directed primarily to surface waters, although much of the foregoing applies equally well to ground waters. Mill wastes are commonly stored in tailings ponds, and the opportunity thus exists for contamination of ground waters by seepage of the pond contents downward toward water-bearing strata. Pollution of this type where the ground waters are used or are usable can be quite significant because of the permanency of ground water contamination. Once the discharge of contaminants to surface waters ceases a fairly rapid recovery of the stream to its former quality can be expected; this is not the case, however, with ground waters. Suspected cases of ground water contamination due to seepage from mill tailings ponds have been reported[3, 4] where dissolved radium concentrations significantly above background levels have been found at test well depths to 95 feet.

In another instance [35] nitrate pollution of ground waters by seepage from tailings ponds was demonstrated. The 3.9 tons per day of nitrates (as N) contained in wastes from a resin-in-pulp mill caused observable contamination of shallow ground waters at distances up to 6.3 miles from the mill. It was estimated that 87 percent of the waste volume discharged to a 70-acre tailings pond, which had no surface overflow, was lost by seepage at the rate of 0.17 feet per day. The possibility of significant ground water pollution in the vicinity of uranium mills should not be overlooked.

PHYSICAL POLLUTANTS

In addition to the radioactivity contributed to the stream by discharged ore tailings, as discussed previously, these spent

ore solids can smother the bottom organisms normally found on the bed of an unpolluted stream. The aquatic insects, algae, and other organisms living on the river bottom are important sources of food for fish life. The depostition of ore solids in the stream can cause a marked decrease in productivity of bottom-dwelling fish food organisms by blanketing the stream bottom, thus forming an undesirable physical environment that inhibits their growth. Such a reduction of bottom fauna brings about a corresponding reduction of fish life in the stream.

The discharge of very fine and not readily settleable ore particles, or slimes, causes the receiving stream to become turbid, reducing its suitability as a habitat for biological forms and increasing the difficulty of water treatment for municipal and some industrial uses. Highly colored mill waste streams create aesthetically objectionable conditions in the receiving stream. In a number of cases it has been observed that the release of low pH effluents (pH of 1.0 to 2.0) to the slightly alkaline stream has resulted in the formation of a fine floc that may persist for miles and is most unsightly.

POLLUTION

ABATEMENT METHODS

The preceding discussions of the pollutional capabilities of uranium mill wastes clearly indicate the necessity for containment of certain wastes and treatment of others prior to discharge to surface waters. Treatment for reduction of radium, both dissolved and suspended, is of primary importance to minimize human internal radiation exposure. Waste treatment to protect the biological life of the receiving stream is necessary and interference with legitimate uses of the down-stream waters, such as municipal, industrial, or irrigation water supply, must be prevented.

Waste treatment and control practices in the uranium industry have improved greatly during the past 5 years. Direct radium-226 pollution or the release of undesirable chemical wastes at significantly high levels occurs in only a few isolated cases. Other more subtle problems such as the leachability of radium-226 from tailings and refinement of waste treatment practices are under study. It is now general practice throughout the uranium industry to retain wastes in tailings ponds, or lagoons, and this single measure is of real value in preventing many of the potential water damages discussed in previous sections. Under these conditions settleable waste ore solids are retained at the mills and the total amount of radium entering the country's rivers is kept to a low level, most certainly far less than the estimate of 1000 curies per year which was made recently.[38] This is readily apparent since all of the radium dissolved by the milling industry amounts to less than fifty curies each year and even a large majority of this is not discharged to surface waters. Additional waste treatment measures are often required, however, and these are discussed in detail below.

The Atomic Energy Commission, under whose licensing authority the uranium mills operate, has established limits

for the radioactivity content of liquid effluents discharged by the mills.[32] These limits, expressed as radioisotope concentrations in the effluent before release, are one-tenth of the MPC values given in the National Bureau of Standards Handbook 69 for continuous occupational exposure limits.[13] In addition, the regulations provide for the possibility of higher concentrations in the effluent at a particular mill if it can be demonstrated that it is not likely that any individual will be exposed to radioisotope concentrations greater than the prescribed limits. In the issuance or renewal of Source Material Licenses for uranium mills, the Atomic Energy Commission indicates what exceptions to the prescribed limits have been approved. The license also contains additional specific discharge requirements. These additional requirements now call for effluents to be substantially free of settleable solid materials and may also limit volumes to be discharged. Requirements for frequency of reporting on analysis of waste flows and receiving waters and maintenance of data records are also usually stated in the Atomic Energy Commission license.

Thus, the Atomic Energy Commission regulations provide guidelines for mill operators in carrying out pollution abatement measures. The ultimate test of the success of such measures, however, is the maintenance of receiving waters at a level which permits the full development of all legitimate downstream water uses. In addition, the total radiation exposure of downstream populations from all man-made sources must remain within prescribed limits and should be minimized to the greatest feasible extent.

TAILINGS PONDS

A universal minimum treatment step for mill wastes is the impoundment of liquid-borne wastes in ponds. These ponds, which are used to retain solid ore residues (tails), are usually referred to as tailings ponds. Because of the large amount of solids or tailings to be handled, the peripheral dikes of many such ponds are in fact composed of the tails material itself. These ponds gradually fill with solids and in this manner they tend to "grow" in size and/or elevation. The original dam or dike behind which the slurried tailings are retained is often of earthen construction. The tailings solids which accumulate behind this dike are then used to extend the tickness and height of the earthen dam until ultimately they become its major constituent. In practice, advantage is taken of the more readily sep-

arable coarse sands for use in covering the exterior surface of the dam, thus leaving the slimes to settle out of the slurry and form the interior surface of the dam wall. Excessive use of uniformly sized tails in any one portion of the dam wall leads to instability and should be avoided.

The amount of overflow from the tailings ponds is a function of net liquid input and the evaporation and seepage which occur. It is not uncommon for these ponds to produce no overflow for long periods of time, or in some cases, indefinitely. Where extensive land area is available, advantage is taken of natural ground contours to create ponds or lagoons which may be as large as 300 acres.

As a minimum accomplishment, such ponds can successfully remove substantially all settleable solids. In addition, they serve as reservoirs for water which may be recycled to the mill process, thereby reducing the total water consumption and the quantity of liquid waste for disposal, minimizing the required pond area. Tailings pond water is commonly used to repulp the waste tails filter cake that results from the last stage of liquid-solids separation following alkaline leaching. Although this procedure reduces significantly the net quantity of liquid to be disposed of, the daily quantity of dissolved radioactivity, as well as most other dissolved contaminants produced in the milling process, remains unchanged. As a result the concentration of dissolved radium and other constituents tend to build up to higher levels in tailings ponds where recirculation is practiced.

At two alkaline mills,[3,4] for example, though the dissolved radium leaving the mill process was found to be negligible during the period of the mill survey, the dissolved radium content of the tailings pond water was 35 micromicrocuries per liter in one case, and 160 in the other. Dissolved radium concentrations in tailings pond waters can be expected to vary greatly, even among mills using the same process. In addition to recirculation, this variation is brought about by differences in the raw ore, size of ponds, evaporation rates, mill solution bleedoff rates and other factors, including coprecipitation of radium. Thus, although the daily quantity of dissolved radium wasted from a given milling process may be expected to be in a relatively narrow range on a per ton basis, the actual concentration in the tailings pond discharge (overflow or seepage) may vary greatly among them.

The waste ore slurry is pumped to a tailings pond where the solids are separated and retained.

One of the industry's most extensive tailings pond areas is shown above. In this case liquid is decanted from the pond and injected into a deep well for ultimate disposal. (Photograph courtesy of The Anaconda Company)

The light-colored tailings pile dominates this scene. Wind-blown particles of waste ore solids may be scattered over a wide area.

Waste tails are pictured next to an abandoned uranium mill. The Colorado River flows by at the right. Permanent retention of such solids is a most important pollution control measure.

It may be noted at this point that the only liquid waste resulting from the alkaline-filtration process is the moisture contained in the final tails filter cake, which is usually about 80 percent solids. Instead of repulping this relatively dry filter cake with additional water (fresh or recirculated), it could be disposed of as a solid waste. It appears probable that the slight moisture which these solids contain would be lost rapidly through evaporation, thereby eliminating the liquid waste problem for this type of mill.

As noted previously, the amount of liquid overflow from tailings ponds is dependent upon the amount of inflow, the net liquid loss or gain from rainfall and evaporation, and losses from seepage. Reduction in the amount of dissolved pollutants which may be discharged, however, is affected primarily by seepage. The output of dissolved radioactive isotopes could actually increase if significant amounts are leached from the waste tails during the contact period in the pond. Volume reduction by seepage is desirable except where ground water pollution is of significance. In this event, steps to prevent seepage, such as lining the pond bottom, may be required.

Tailings ponds, then, are beneficial as a pollution abatement measure in several ways, including (1) removal of settleable solids; (2) recovering water for reuse; (3) permitting evaporation; (4) providing opportunity for seepage, thereby reducing the amount of pollutants which reach the receiving stream; (5) retaining wastes during dry periods of low stream flow for release during high flow periods when greater dilution is available; and (6) retaining radioactive pollutants, temporarily permitting the decay of shorter-lived materials.

Undesirable features of such ponds are (1) the inherent porosity of the tails, permitting seepage laterally or vertically; (2) the prolonged contact between the liquid and the tails, providing the opportunity for continued leaching of radioactive contaminants; and (3) their observed tendency to fail structurally and release their contents, if the walls are not properly constructed or maintained.

Where it is found necessary to minimize seepage, measures to reduce the porosity of the pond bottom and sides is required. Minimization of contact between the liquid and the waste solids could be achieved by providing two or more ponds

GPO 825880-7

in series. Removal of settleable solids could be accomplished in the first pond if a short liquid detention period is provided. The overflow from this pond could then be contained for further evaporation (and seepage if desirable) in a second, larger pond with dikes constructed of material other than tails.

The problem of tailings pond dike failures is a most significant one. Accidental releases of mill tailings pond contents to the environment by this means have occurred at several mill locations during the past 10 years.[28] In a recent instance, a considerable volume of highly acid liquor with a high radium concentration spilled from a storage pond to an adjacent river over a period of a few hours. It is estimated that as much as 1 millicurie of dissolved radium-226 may have been released. Some portion of this dissolved radium probably precipitated as a result of neutralization of the waste by the stream alkalinity. Evidences of an extensive fish kill due to chemical toxicity were observed downstream of the mill immediately following the spill. Although downstream river uses included municipal water supplies, it was concluded that significant human over-exposure to radiation did not occur because of the short duration of the release, the quantity of radium released, and the available dilution afforded by the prevailing river flow. Considerably lower flows in this stream and others adjacent to uranium mills are common, however, so that dilution of the released material could have been much less under other circumstances.

Such accidental releases present a distinct hazard to downstream aquatic populations and a potential hazard to humans. Accordingly, appropriate measures should be taken to preclude their occurrence. A protective secondary dike surrounding the tailings pond area would, if properly designed and constructed, contain wastes accidentally released by tailings pond dike failures and prevent their entrance into nearby surface waters. Such a dike would also prevent the washing away of tails by excessive surface water runoff. This or similarly reliable measures should be employed.

CHEMICAL TREATMENT

Waste Neutralization

The relatively simple step of neutralization is quite effective in reducing the pollutional potential of acid leach mill wastes. In addition to eliminating the quite significant harm-

ful effects of excess acidity on the aquatic life of a receiving stream, the solubility of certain radioactive and chemical pollutants is greatly reduced, causing their precipitation and subsequent retention in the waste ponds.

Of greatest significance is the removal of dissolved radium in acid leach effluents by neutralization to a pH of 7.0. An 83 percent reduction was observed at one mill[5] and slightly higher values to (90%) have been reported elsewhere.[20] In addition, the dissolved thorium would be precipitated. The concentrations of certain chemicals in solution, such as sulphate, phosphate, iron, copper, cobalt, arsenic, uranium, and vanadium, likewise are reduced by neutralization. Lime is most commonly used as a neutralizing agent.

The addition of sulfuric acid to alkaline mill wastes for pH reduction may also bring about some removal of soluble radium.[20] The extent of removal observed in bench-scale laboratory tests was variable, however. The observed removals probably resulted from the presence of finely divided solids and precipitates formed during neutralization, and the mechanism of dissolved radium removal was adsorption onto solid particulate surfaces. Because of this tendency of radium to be bound to the finer solid particles, the best sedimentation practice is required following neutralization if maximum removals are to be achieved.

At a few mills both acid and alkaline leaching of ores is practiced. At these mills combination of the respective acid and alkaline waste streams is an obvious and practical treatment step.

Barite Treatment

A reduction of dissolved radium in acid leach wastes by a factor of ten, as obtained by neutralization, is often insufficient to meet discharge requirements, and further treatment steps may be required. One procedure which has been found effective for dissolved radium removal employs the crude mineral form of barium sulfate, referred to as barite. This material has been tested on a pilot scale and is presently in use at several mills.

Soluble radium removals up to 90 percent and higher by barite treatment have been obtained in bench-scale tests of neutralized acid and alkaline mill wastes.[20] The amount of

removal actually achieved was found to be dependent primarily upon the mesh size of the barite, the intimacy and time of contact, and the method of application. The most efficient treatment procedure is to percolate the waste through a column of barite, which results in a chemical consumption of about 300 milligrams of barite per liter of waste treated and results in an apparent radium-226 removal in excess of 90 percent. Treatment may also be carried out by percolation of the liquid waste through a shallow bed of barite, or by batch treatment in which the barite is added to the waste in agitated or quiescent tanks. The barite requirements for this latter mode of treatment are higher for comparable radium removals and recycling or series treatment may be necessary. Thus the combination of acid mill waste neutralization, which can remove up to 90 percent of the dissolved radium, followed by barite treatment where an additional 90 percent removal may also be possible, would result in an over-all removal of 99 percent or a reduction in soluble radium content by a factor of 100.

Various methods of barite treatment are now being used by several mills to determine whether the laboratory findings previously described are as effective in full-scale applications. There is some indication that a more refined form of barium, i.e., barium carbonate or barium chloride, may be a more effective treatment agent, with little or no increase in the cost of treatment. The total cost of chemicals for the neutralization-barite treatment for acid mill wastes is estimated to be about 20 to 40 cents per ton of ore processed, 80 to 90 percent of which represents the cost of neutralization.

An effective treatment for dissolved radium removal from alkaline leach mill waste liquids has been found in laboratory tests with copperas ($FeSO_4 7H_2O$) as a flocculating agent together with barite.[20] A two-step treatment, in which copperas is added in the first step followed by two-settling stages and barite is added in the second step, yielded over-all removals of 97 percent. This level of removal would ordinarily result in a treated effluent which meets Atomic Energy Commission limits for dissolved radium-226, if it is as effective in full-scale mill operations as in tests.

Raffinate Treatment

In discussions of the pollutional effects of mill wastes, the organic-bearing raffinate from the solvent extraction process

Organic-bearing raffinate is stored in ponds of this type. Because of its toxicity to aquatic life, this material should be disposed of by seepage or treated prior to discharge.

has been cited as the most toxic to aquatic life. This waste contains significant quantities of both the costly solvent and its diluent, kerosene, and is highly acidic. Because of the nature of the waste, it may be impounded separately in retention ponds, as has been done in at least one case,[8] from which evaporation or seepage may be sufficient to preclude its overflow. Prior to entering the ponds this waste usually is passed through a holding tank to permit any possible further recovery by skimming. An added treatment step for further entrained organic removal which suggests itself at this point is the addition of make-up kerosene. The additional organic removed as a result could be recycled to the uranium extraction process with attendant savings in solvent cost. Such extra kerosene could easily be added in a small flash mixer ahead of the holding tank, and no loss of the diluent should result since the waste is undoubtedly fully saturated and charged with kerosene on leaving the extraction tank. Even more thorough treatment could be provided by vacuum or pressure flotation procedures.[33] For instance, air could be dissolved under pressure in the raffinate by inserting a pump and small pressure tank ahead of

the decantation tank. Air and excess kerosene could be added at the suction side of the pump. Upon reaching the decantation tank, the dissolved air would come out of solution as minute bubbles which, in rising to the surface, would tend to separate the immiscible kerosene and solvent present. These materials could be skimmed off for return to the uranium extraction process. Any solvent dissolved in the raffinate rather than entrained would be unaffected, however.

Very little dissolved radium is extracted by the solvent, and the treated effluent from the decantation step would still contain substantial quantities (See Figure 10). This effluent, if treated as outlined above, could then be impounded separately or added to the tailings pond contents for further treatment for dissolved radium removal.

DEEP-WELL INJECTION

The Anaconda Company at Grants, New Mexico, recently put into operation a deep-well injection system for disposal of tailing water from its acid-leach, resin-in-pulp mill. The injection well was drilled to 2511 feet with an original diameter of slightly less than 8 inches. The disposal zone extends downward from 950 feet for a distance of almost 600 feet.

The acidic waste waters are decanted from the tailings pond, treated with copper sulphate (for slime control) and a sequestering agent, then passed through circular leaf filters for turbidity removal. The treated waste is injected into the well by gravity at a rate of 400 gallons per minute. The static water level of 240 feet provides a natural hydrostatic injection pressure of about 100 pounds per square inch.

Upon entry of the waste water into the underground formation, neutralization, precipitation, ion exchange, and dilution by the ground waters take place. Calculations of the porosity and ion-exchange capacity of the sands in the disposal formations indicate a useful life expectancy of the system of more than 10 years.

Special care has been taken in casing the well to prevent the possible contamination of the major potable water aquifer at a higher elevation. A monitoring well has been located in this aquifer some 300 feet away in the direction of the hydraulic gradient. Weekly samples have indicated that no leakage is taking place. A regional monitoring program of all fresh water

sources in a 20-square-mile area surrounding the well has also been instituted.

The successful operation of this deep-well injection system is most encouraging and points the way toward what may be one of the most satisfactory available methods for disposal of liquid mill wastes.

SOLID WASTE DISPOSAL

The methods of waste treatment discussed above have as their objective the conversion of dissolved radioactivity, specifically radium, to an insoluble form which can be precipitated from the waste solution prior to discharge. The radium thus removed from solution, together with the large amount of solid ore tailings, is retained in ponds while the treated liquid is disposed of by evaporation, seepage, and/or discharge to surface waters. These retained solids contain a considerable quantity of radium, all but a minute fractional percentage of that originally present in the raw ore. Hence, the tailings piles represent a great reservoir of potential radium contamination of nearby surface and ground waters and must be controlled accordingly. The magnitude of this reservoir is indicated by the amount of tailing solids accumulated to date, which is estimated to be 34 million tons.[12]

The radium contained in these solids is known to be leachable by contact with water. This is especially true of the precipitated solids from neutralization and barite treatment processes. Therefore, these solids should not be permitted to enter natural bodies of water. Heavy rainfall, flooding of nearby streams, and wind erosion of the dry tailings piles all present opportunities for the movement of these materials into the aquatic environment. Excessive seepage from the base of such tailings piles provides an early indication of potential structural failure of the wall. Whatever measures are needed at any particular mill site to prevent such movement, should be carried out. These measures may include, for example, the avoidance of flood plains, river banks, and dry wash areas as locations for tailings piles and the construction and maintenance of pond dikes to preclude their rupture due to the hydraulic head within the pond. Cementation of the exterior surfaces of abandoned tailings piles is worthy of consideration at some locations to minimize wind-borne dust. Abandoned mines may make a

suitable long-term repository for waste tailings solids, and this method of disposal, as practiced elsewhere in the mining industry,[34] may of necessity receive more attention in the future. Proposals have been made to use these tails as land-fill material for highway and other construction projects. A thorough evaluation of possible hazards associated with this means of disposal, which would be required in each case, has not been made to date. This type of containment of waste tails, however, may merit further study. The indiscriminate use of tailing sands by nearby residents in concrete, mortar, or plaster mixes, for children's sand boxes or as a garden soil additive should certainly be prevented, for obvious reasons.

It must be emphasized strongly that any steps taken toward reduction of the dissolved radioactivity entering a stream will have been to no avail if the radioactive solids are not permanently controlled. The half-life of radium, 1620 years, clearly indicates the importance of permanent retention and control of this solid waste material.

SUMMARY AND CONCLUSIONS

URANIUM MILLING INDUSTRY

The extraction of uranium from its ores has become a major industry in the United States since the end of World War II. The United States now ranks as the world's largest producer of uranium ore, and of uranium concentrate, the final product of the milling process. The location of major ore deposits is largely centered in the Colorado Plateau and Ambrosia Lakes areas and in Wyoming, with the result that most of the industry's milling capacity is located in the Colorado River Basin and the Grants, New Mexico, area.

The most significant waste materials from this industry are the radioactive daughter products of uranium-238, each of which is found in uranium ores at or near the same level of activity as the parent isotope. The greatest human internal hazard of the 14 radioisotopes in the decay series is presented by radium-226, a long-lived alpha emitter. Of the 264 radioisotopes considered by the ICRP-NCRP, the maximum permissible concentration in water (MPC_w) consumed by the general public is lowest for radium-226, that is, 3.3 micromicrocuries per liter. The next most hazardous isotope is lead-210, which has an MPC_w of 33.3 micromicrocuries per liter. Thorium-230 and uranium-238, whose MPC_w's are 200 and 4,000 times higher, respectively, than radium, have also received attention as radioactive pollutants having potential significance in uranium mill wastes.

Uranium mills employ acid or alkaline leaching to dissolve the uranium content of the ore following grinding. Once the uranium has been put into solution, it is recovered by chemical precipitation, which, in some cases, is preceded by a concentration step in which ion-exchange or solvent-extraction methods are used. The liquid and solid wastes from these operations contain potentially hazardous amounts of radioactive materials, as well as chemical water pollutants which are undesirable from a toxicological, aesthetic, or economic standpoint.

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PROCESS WASTES

During acid leaching about 0.5 percent of the radium-226 content of the ore is usually dissolved and discharged in the mill waste streams. Alkaline leaching has been found to dissolve a greater amount of radium-226 or about 2 percent of that present in the ore. However, in this case, essentially all of that dissolved is precipitated together with the uranium and leaves the mill in the final concentrate product. The radium which is not dissolved during processing leaves the mill as waste in the spent ore.

Uranium and thorium have been shown to be of much less significance as water pollutants than radium-226. Little is presently known of the possible significance of lead-210 as a radioactive pollutant in uranium mill waste discharges.

Chemical constituents of mill wastes are of concern in some instances. Chlorides, nitrates, sulfates, hardness, total dissolved solids, manganese, iron, lead, arsenic, fluoride, organics, and possibly other materials may be present at relatively high levels in uranium mill wastes, depending upon the particular raw ore composition, the milling process, and the chemical reagents used during processing.

POLLUTIONAL EFFECTS

Where uranium mill wastes containing radioisotopes, especially radium-226, are allowed to enter adjacent surface waters, a human internal radiation hazard is presented to downstream water users. This hazard arises from ingestion of radioactive materials in drinking water, and in crops irrigated with contaminated water, and from ingestion by other routes involving animal feed crops such as hay and alfalfa. The degree of hazard is directly related to the amount of both dissolved and undissolved radium discharged to the stream. Spent ore tailings contain virtually all of the radium originally present in the ore and are important reservoirs of potential contamination. If discharged to streams, these solids settle to the bottom where their radium content is gradually leached into the overlying waters.

Liquid mill wastes, particularly the raffinate from solvent extraction mills, are capable of causing severe destruction of the aquatic life in streams. The excess acidity of certain mill

wastes can produce similar effects. The other chemical pollutants mentioned above as being present in mill wastes are also capable of impairing the stream's usefulness as a source of municipal water supply.

Many of the undesirable effects described apply equally to ground waters. Vertical seepage of liquid mill wastes from holding ponds to the ground water table has been demonstrated, resulting in excessive chemical and radioisotope concentrations in water drawn form nearby test wells. The extent of underground travel of these pollutants has not been completely established.

MILL WASTE TREATMENT

Impoundment of mill wastes in tailings ponds is widely practiced in the industry. With proper operation and maintenance of such ponds, it is possible to greatly restrict discharges to nearby streams, depending upon the size of ponds in relation to mill waste output and meteorological and soil conditions. These ponds, in addition, are usually successful in removing most settleable solids. The dikes of many such ponds are made of uncompacted tailings solids, resulting in lateral seepage from the pond and occasional dike failure with the loss of pond contents to the environment.

Mill waste neutralization is an effective treatment step which can bring about dissolved radium reductions of up to 90 percent. Further treatment of neutralized wastes by the addition of barium compounds makes additional reductions of dissolved radium possible.

Organic-bearing raffinate may be impounded separately to allow for evaporation and vertical seepage into the ground. In this way discharge to surface waters with attendant harmful effects on the aquatic biota can be avoided.

CONCLUSIONS

The uranium milling industry is a major potential source of radiological pollution of the aquatic environment. The magnitude of mill operations and the particular isotopes involved present a very real potential threat of excessive human internal radiation exposure. It is only by employing the most careful and deliberate waste control measures that this potential threat can be prevented from becoming an actuality. Improvements in

presently available waste treatment and control procedures should continue to be pursued; however, existing methods, if carefully applied, can provide a reasonably adequate degree of protection.

During the past 5 years the uranium milling industry has made substantial improvements in waste-handling and disposal procedures. As a result, environmental contamination in the vicinity of many mills can be considered to be near a desirable minimum level. Sound radiation protection philosophy dictates, however, that wherever additional reductions in the amount of activity released to the environment can be obtained by reasonable means such reductions should be accomplished. In addition, continued study of the more subtle areas of possible or potential contamination is warranted. Chemical or radiological pollution of ground waters by uranium mill wastes has been shown to occur, for example, and continued investigation of this problem is desirable. In addition, the importance of lead-210 as a mill waste constituent should receive attention.

The extremely long half-life of the major radioisotope involved, that is, radium-226, whose half-life is 1620 years, means that permanent control of ore residues is required. Acceptable methods of very long-term storage and retention, therefore, need to be found. Reliable measures to preclude the accidental release of tailings pond contents and waste ore solids are also needed. Finally, continuous monitoring of the environment is necessary to ensure that waste treatment and confinement methods are producing the desired results.

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